# INSTITUTE NOTES.

MARCH 1940.

TELEGRAPHIC ADDRESS

Telegrams and cablegrams for the Institute may be addressed:
**Instpetech Birmingham.**

The telephone number of the Institute is: Birmingham, Selly Oak 1181 (Extension 5).

## FORTHCOMING MEETINGS.

Tuesday, 16th April, at 6.45 p.m. At the Chemical Society's Rooms, Burlington House, Piccadilly, London, W. 1.

**"The Manufacture and Testing of Roofing Felts and Damp-courses,"** by Major D. M. Wilson.

Meeting of the Asphaltic Bitumen Group.

## CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Fellow, Member or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

BRADFORD, Job Ronald Tremellen, Representative, Aviation Dept., Shell-Mex & B.P., Ltd., Victoria Embankment, London, W.C.2. (*A. E. Hope ; F. N. Harrap.*)

CLARKE, Geoffrey Jardine, Student (*Royal School of Mines*), 5, The Grove, Aberdare, Glam. (*S. E. Coomber ; G. D. Hobson.*)

EISNER, John Hans, Engineer (*Lobitos Oilfields, Ltd.*), Dol-y-Wern, Great Sutton, Cheshire. (*J. S. Parker ; J. C. Wood-Mallock.*)

GASCOIGNE, George Norman, Director (*Anglamol, Ltd.*), 34, Grove Way, Esher, Surrey. (*E. A. Evans ; H. C. Tett.*)

GREIG, Alan Lancelot, Geologist, c/o Midland Bank Ltd., Gloucester Road, London, S.W.7. (*S. E. Coomber ; G. D. Hobson.*)

HIGGS, Percival George, Chemist, c/o Anglo-Egyptian Oilfields, Ltd., Suez, Egypt. (*J. Kewley ; W. K. McGavin.*) (Trans. to Member.)

KENYON, Harold Frederick, Chemist (*Asiatic Petroleum Co., Ltd.*), 13, Victoria Road, Cambridge. (*J. Kewley ; C. H. Barton.*)

ROGER, Arthur, Chemist (*Carbohydrol, Ltd.*), "Leckonby," Whitbarrow Road, Lymm, nr. Warrington. (*J. E. Haslam ; H. O. Clayton.*)

SCHARGES, Walter Herbert, Assistant Superintendent (*Texas Co. (S.A.), Ltd.*), P.O. Box 714, Cape Town, South Africa. (*E. W. Ramsay ; J. W. Weitz.*)

TEMPLE, George Edward Maskell, Chemist, c/o Anglo-Iranian Oil Co., Ltd., Abadan, Iran. (*H. Macniven ; P. W. Wright.*)

TOKAYER, Oscar, Editor (*Petroleum Press Service*), Glenthorne, Links Way, Northwood, Middx. (*J. Kewley ; H. E. Medlicott.*)

## CANDIDATES FOR ADMISSION AS STUDENTS.

PROPOSED BY A. W. NASH, SECONDED BY A. H. NISSAN.

| | | | | |
|---|---|---|---|---|
| AUSTIN, John Martin, | The University of Birmingham, | Dept. of | Oil | Engineering. |
| BUXTON, Geoffrey | ,, | ,, | ,, | ,, |
| CHEETHAM, Harry Alan | ,, | ,, | ,, | ,, |
| CUDE, Arthur Leslie | ,, | ,, | ,, | ,, |
| CHIVERS, Harold Victor | ,, | ,, | ,, | ,, |
| GRUNBERG, Leander | ,, | ,, | ,, | ,, |
| HAWKES, John Cecil | ,, | ,, | ,, | ,, |
| METCALFE, John Leslie | ,, | ,, | ,, | ,, |
| NEILSON, Ian McIntosh | ,, | ,, | ,, | ,, |
| SHACKELL, Douglas Ashton | ,, | ,, | ,, | ,, |
| SIMPSON, Alan Murray | ,, | ,, | ,, | ,, |
| TONGE, Peter | ,, | ,, | ,, | ,, |
| WISEMAN, Kenneth William | ,, | ,, | ,, | ,, |
| WOOD, George Frederick | ,, | ,, | ,, | ,, |

## NEW MEMBERS.

The following elections have been made by the Council in accordance with the By-Laws, Section IV, Para. 7.

Elections are subject to confirmation in accordance with the By-Laws, Section IV, Paras. 9 and 10.

*As Fellows.*

ROTH, Francis ... ... ... ... ... ... Sweden.

*As Members.*

MARSHALL, John Macintosh ... ... ... ... West Kirby.
PARK, James Harris ... ... ... ... ... Birmingham.

*As Associate Members.*

EVANS, Frederick Neville Stuart ... ... ... Reading.
PHIPPS, Leonard Fredrick ... ... ... ... Singapore.

*As transfer to Associate Member.*

HOLLOWAY, Gilbert Lloyd ... ... ... ... Birmingham.

*As Student.*

KHALILI, Jawad ... ... ... ... ... Sunbury-on-Thames.

The following transfers have been approved by Council :—

*From Member to Fellow.*

D. S. PAUL. P. E. SPIELMANN.

ARTHUR W. EASTLAKE,
*Honorary Secretary.*

VOL. 26. NO. 197. MARCH 1940.

# THE FLOW PROPERTIES OF BITUMINOUS MATERIALS.*

A. R. LEE, B.Sc., Ph.D., A.R.C.S., D.I.C., J. B. WARREN, B.Sc., Ph.D., A.R.C.S., D.I.C., A.Inst.P., and D. B. WATERS, B.Sc., Assoc.M.Inst.C.E.

## SUMMARY.

Some results are given of the investigations now in progress on the fundamental flow properties of bitumens and bitumen-aggregate mixtures. A coni-cylindrical viscometer has been used for measuring the effect of stress and temperature on the viscosity and elastic recovery of various types of bitumens. The relation between rate of shear ($D$) and shearing stress ($S$) for all but the most plastic bitumens may be represented by an equation of the form $D = \left(\frac{1}{\eta'}\right)S^p$, where $\eta'$ and $p$ are constants. The use of the index $p$ as a "plastic-flow index" provides a method of expressing the degree of plasticity of a bitumen, where this is considered as the divergence from ideal viscous flow. Different bitumens having the same penetration (65) may have very different viscosities. The bitumens so far investigated have been found to differ chiefly in their plastic and elastic properties.

The effect of stress and temperature on the flow properties of roller-compacted specimens of bitumen-aggregate mixtures has been investigated by beam and tensile tests. The relation between stress ($S$) and minimum rate of strain ($R$) may be expressed by the equation $R = KS^P$, where $K$ and $P$ are constants. The flow properties at the minimum rate of deformation under conditions of constant tensile stress may be expressed completely by a number of constants—namely $P$, $K_0$ (the minimum rate of strain at unit stress at 0° C.), $N$ (the rate of change of log. $K$ with change of temperature), and the extensibility at failure, the value of these constants being determined by the nature and grading of the aggregate and by the nature of the binder. Mixtures of a particular aggregate grading containing the more plastic bitumens have greater values for $P$ than those containing non-plastic bitumen; the value of $P$ is affected more by the grading and proportion of the aggregate than by the nature of the bitumen.

## INTRODUCTION.

BITUMINOUS materials are used for a large variety of industrial purposes, but most extensively in road construction. Although the present paper deals with this aspect of their use, much of the information presented is of more general interest, since it is concerned with fundamental properties. The materials used must be readily adaptable to keep pace with the development of modern industrial methods, and this can be achieved only if the essential properties of the materials are fully understood. Data on the fundamental flow properties of bituminous materials are being obtained with three main objects in view: first, to enable their behaviour in service to be predicted, and thus to enable their suitability for specific purposes to be judged; second, to enable their behaviour during mixing and laying to be predicted, and so to enable the most satisfactory conditions for application to be determined; and third, to provide information on

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the nature of the internal structure of the bitumens themselves, in order to indicate the best method of preparing a binder having any required properties.

In the study of the rheological properties of mixtures of bitumen and aggregate a knowledge of the characteristics of the binders is clearly of first importance. Until recently little was known of the fundamental flow properties of bitumens, although in the testing of bitumens for industrial purposes many different empirical tests involving flow properties have long been used as aids to the selection or specification of materials. Such tests are useful for ensuring that samples of the same material conform to a standard measured under certain arbitrary conditions of flow, but as a true comparison of the behaviour in service of different materials and as a basis for improving and understanding existing techniques they are of little value. In fact, certain of these tests (such as the penetration test), when taken alone, can often be misleading. Moreover, in cases where the measurements are reproducible to a high degree of accuracy, fundamental importance may frequently be attached erroneously to small differences. In general, the tests measure complicated and variable functions of several fundamental properties operating simultaneously. For example, the "penetration" value depends on viscosity, elasticity, tensile strength, and adhesion; and the "ductility" value depends, among other properties, on the viscosity and the internal cohesion. Bingham [1] has pointed out that "the use of such empirical tests which are not based on any sort of theory of the fundamental nature of flow have more than any other thing prevented the progress of the art of rheology." It is probably true to add that it has also retarded the development of the industries using these and other plastic materials.

An investigation has therefore been started at the Road Research Laboratory to correlate the behaviour on the road of bituminous surfacings with the rheological characteristics of their binders and of mixtures prepared in the laboratory. This investigation thus involves initially an attempt to evaluate in absolute units the viscous and elastic properties of both the bituminous binders and the consolidated bitumen-aggregate mixtures.

Simple proportionality between stress and strain or rate of strain is not generally shown by these materials; therefore, the determination of the flow coefficients expressing these relations must be made under conditions of uniform stress. For the bitumens themselves the use of suitable viscometers is therefore necessary; for the bitumen-aggregate mixtures uniform stress distribution across the specimen must also be ensured, involving either the application of a constant stress or a constant rate of strain, whichever is the more convenient. Extensibility, as defined by the percentage elongation of the specimen at failure, and the elastic recovery which occurs on removal of the applied stress are further rheological properties which can be measured by either method of testing. Such concepts as the coefficient of viscosity or the moduli of elasticity and of rigidity are the results of experiment applied on the one hand to substances definitely in the liquid state, and on the other to those in the truly solid state. It is not, therefore, to be expected that the linear relationship between stress and strain or rate of strain implied by using such moduli

will necessarily apply to these more complicated materials, which may exhibit both solid and liquid properties at the same time.

When the stresses are rapidly applied, as in the case of impact or vibration forces from passing vehicles, bitumen-aggregate mixtures exhibit the properties of solids. Some progress has been made in measuring the transient forces normally occurring on the road, and it is important to investigate the relation between stress and strain for bituminous materials under similar conditions of rapid stress application. The stresses applied by most impact tests are usually of a high, but indeterminate, order, making

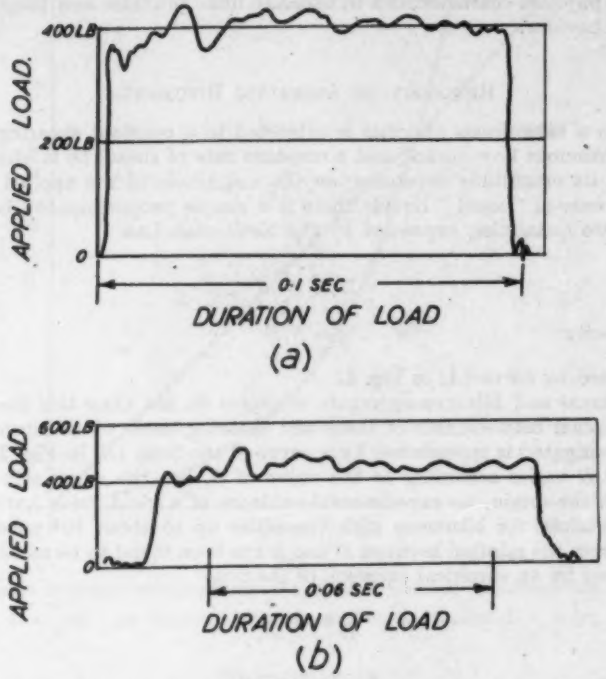



FIG. 1.

LOAD–TIME CURVES GIVEN BY REPEATED TRANSIENT LOAD TESTING MACHINE.

it impossible to determine the fundamental rheological properties involved, and it is open to question whether such tests reproduce practical conditions, or have any practical significance. A machine has therefore been constructed which subjects bituminous specimens to a repeated, suddenly applied, transient stress of a given value maintained approximately constant for a short predetermined time. The stress–strain relations can thus be evaluated for "impact" forces of known magnitude and duration (of the order of $\frac{1}{10}$ to $\frac{1}{50}$ second) which are repeated at intervals of one second to half a minute. Typical load–time curves given by the machine are shown in Fig. 1. Conditions of stress similar to those beneath the wheel of a

passing vehicle are thus obtained, but forces arising from vibration are not supplied. The extension of the measurements to the elastic properties exhibited under vibrations of audio-frequency would complete the field of investigation of the rheological characteristics of bituminous materials necessary for deducing the stress–strain–time relations met with in practice. Some measurements on these lines have already been reported.[2, 3]

Examples of the results of the investigations now in progress on bitumens and on bitumen-aggregate mixtures are given below, and serve to illustrate that, although these problems are complicated, the evaluation of the fundamental physical characteristics in absolute units provides new insight into their behaviour.

## Rheology of Asphaltic Bitumens.

When a bituminous material is subjected to a constant shearing stress ($S$), continuous flow occurs, and a constant rate of shear ($D$) is ultimately set up, its magnitude depending on the magnitude of the applied stress. In the case of "ideal" liquids there is a simple proportionality between these two quantities, expressed by the Newtonian Law

$$D = \left(\frac{1}{\eta}\right)S$$

or viscosity

$$\eta = S/D$$

illustrated by curve ($A$) in Fig. 2.

Bitumens and bitumen-aggregate mixtures do not obey this ideal law. The relation between rate of shear and shearing stress of all bitumens so far investigated is represented by a curve of the form ($B$) in Fig. 2. The ratio $S/D$ varies according to the value of $S$, but the curve still passes through the origin, no experimental evidence of a yield value having yet been obtained for bitumens with viscosities up to about $10^8$ poises. In these cases the relation between $D$ and $S$ has been found to be more nearly expressed by an empirical equation of the type

$$D = \frac{1}{\eta'}S^p,$$

where $\eta'$ and $p$ are constants, $\eta'$ resembling (but not in dimensions) the viscosity $\eta$ in the earlier equation. As pointed out by Scott Blair,[4] this equation has been found by many investigators to apply to a great number of materials. It has as yet no theoretical significance, but provides a convenient means, at the present stage of rheological knowledge, of expressing the flow-curves in terms of certain numerical constants.

For a satisfactory evaluation of the rate of flow–stress–temperature relations, such materials must be subjected to a range of uniform shear stresses of known values at various known temperatures. Further, the rate of shear under constant stress generally varies for some time after the initial application of the stress, and the material must undergo some continuous deformation before the rate of shear becomes constant. The rotating cylinder viscometer, which gives a closer approximation to these

conditions than any other viscometer, has been found most satisfactory for these investigations.

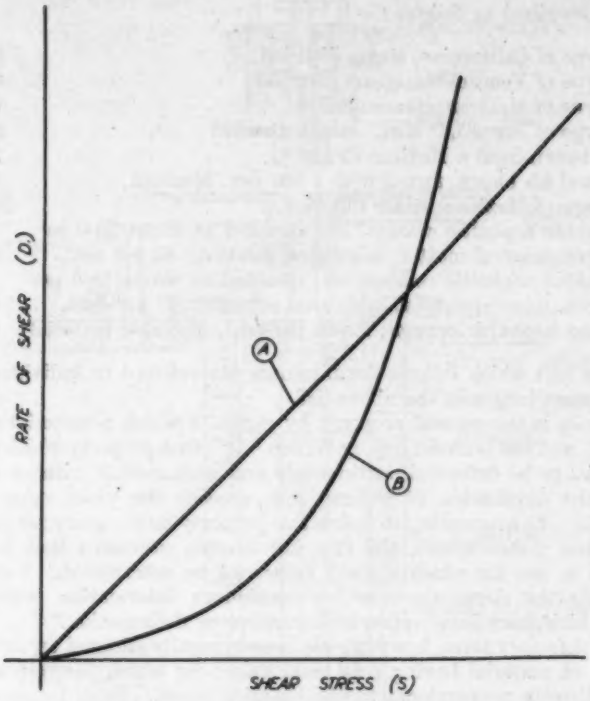



FIG. 2.

RELATION BETWEEN SHEAR STRESS AND RATE OF SHEAR. (A) IDEAL RELATION ($D = \frac{1}{\eta} S$). (B) RELATION FOR BITUMINOUS MATERIALS ($D = \frac{1}{\eta} S^p$).

## NOMENCLATURE.

Owing to certain difficulties that arise when considering some of the results of these investigations, attention is directed to the terminology which has been adopted.

The scientific description of naturally occurring products frequently presents some measure of difficulty. Obviously no one would regard "British coal" as a clear scientific description. Similarly, it is inaccurate and misleading to refer to "Californian bitumen," since several types of crude oils occur in the large area of California. On the other hand, a fuller description associating any particular oil with the well from which it was obtained at a particular date would not be any more helpful, since such a description would only be imperfectly understood even locally. In the circumstances the best that can be done is to refer to the products under

consideration as "a type of Californian bitumen," etc., and to rely upon the chemical data to supplement the description.

The asphaltic bitumens and asphalts dealt with in this paper will therefore be described as follows:—

| | | |
|---|---|---|
| A. | A type of Californian, steam distilled . . . . . | 65 pen. |
| B. | A type of Venezuelan, steam distilled . . . . . | 65 „ |
| C. | A type of Mexican, steam distilled . . . . . | 65 „ |
| D. | A type of Borneo, "Miri," steam distilled . . . . | 65 „ |
| E. | Air blown from a Mexican Crude . . . . . | 22 „ |
| F. | Fluxed air blown, fluxed with a 200 pen. Mexican . . | 65 „ |
| G. | A type of Mexican, steam distilled . . . . . | 200 „ |
| H. | Trinidad asphaltic cement, 5A, specified as about 23·0 per cent. mineral matter, calculated solubility 62 per cent. . | 65 „ |
| I. | Trinidad asphaltic cement, 5B, specified as about 18·5 per cent. mineral matter, calculated solubility 77 per cent. . | 65 „ |
| J. | Cuban asphaltic cement, 22–24 per cent. insoluble material | 65 „ |

In the text which follows the bitumens are referred to individually by the reference letters in the above list.

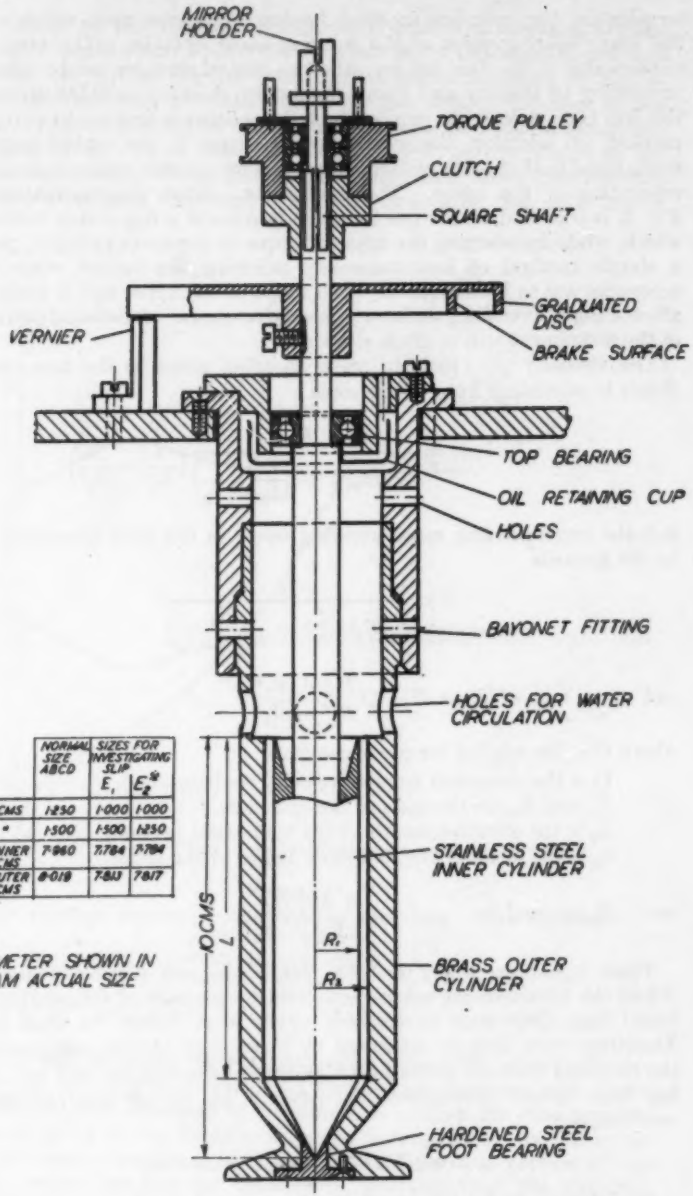
*Plasticity* is the general property by virtue of which a material may be moulded, and has been defined by Wilson [5] as "that property which enables a material to be deformed continuously and permanently without rupture during the application of a force that exceeds the yield value of the material." In attempting to define this property more rigidly for purposes of physical measurement, the idea has become prevalent that a plastic material is one for which a yield value can be determined. This value represents the stress above which continuous deformation occurs, and below which there is no appreciable continuous deformation.[6] *

No satisfactory term, however, has been generally adopted for describing a liquid (a material having zero yield value) for which the rate of shear is not directly proportional to the shearing stress. Such terms as non-Newtonian flow, pseudo-plasticity, quasi-viscosity, and structural viscosity have been employed, but they become inconvenient when used to compare materials which differ in their degree of deviation from ideal flow. It has consequently been found desirable, in order to preserve a reasonable degree of clarity, to refer to the plastic flow of such materials even though they have a zero yield value. It is considered that if such an artificial division is necessary, the term plastic solid should be applied to materials having a definite yield value and the term plastic liquid to those which do not. With many plastic solids the yield value is indefinite and the classification depends largely on the sensitivity of the measurement or on the choice of an arbitrary minimum yield stress such as gravitational stress.

### The Coni-Cylindrical Viscometer.

A viscometer similar to that used by Saal [7] has been used. In this instrument the difficulty of estimating the lower end effect is overcome by

* Roller distinguishes between plasticity, which depends on the actual magnitude of the deformation, and plastic flow, which depends on the rate of deformation.




| | NORMAL SIZE ABCD | SIZES FOR INVESTIGATING SLIP $E_1$ | $E_2^{\frac{1}{10}}$ |
|---|---|---|---|
| R. CMS | 1·250 | 1·000 | 1·000 |
| $R_2$ " | 1·500 | 1·500 | 1·250 |
| L INNER CMS | 7·960 | 7·784 | 7·794 |
| L OUTER CMS | 8·019 | 7·843 | 7·817 |

* VISCOMETER SHOWN IN DIAGRAM ACTUAL SIZE

FIG. 3.

CONI-CYLINDRICAL VISCOMETER.

terminating the cylinders in cones having a common apex which acts as the lower bearing point of the rotating inner cylinder. The viscous resistance due to the fluid between the two conical surfaces can be calculated (according to Mooney and Ewart [8]), and by choosing suitable dimensions this has been reduced to one tenth of the resistance due to the cylindrical portion; in addition, the mean shearing stress in the conical portion is made equal to that in the cylindrical portion by suitable choice of the angular separation of the cones. The instrument, shown diagrammatically in Fig. 3, is provided with a quick release brake and a dog-clutch mechanism which, while transferring the applied torque to the inner cylinder, provides a simple method of instantaneously releasing the torque when elastic recoveries are to be measured. The shape of the upper end is designed to allow a slight overfilling without appreciable errors. A detailed description of the instrument will be given elsewhere.

The viscosity (*i.e.*, ratio of mean shearing stress to the mean rate of shear) is calculated from the formula

$$\eta \text{ (poises)} = \frac{G}{4\pi\Omega L_0\left(1+\frac{R_0}{3L_0\sin\theta_0}\right)\left(\frac{1}{R_1^2}-\frac{1}{R_2^2}\right)}$$

and the corresponding mean shearing stress in the fluid annulus is given by the formula

$$S = \frac{G}{2\pi R_0^2 L_0\left(1+\frac{R_0}{3L_0\sin\theta_0}\right)}$$

and mean rate of shear $D = \Omega\dfrac{R_2^2+R_1^2}{R_2^2-R_1^2}$

where $G$ is the applied torque (dyne cm.),
$\Omega$ is the measured angular velocity (radians/sec.),
$R_1$ and $R_2$ are the radii of the cylinders,
$L_0$ is the effective length of the cylindrical portion,
$\theta_0$ is the mean of the half apex angles of the cones,

and $R_0$ is equal to $\sqrt{\dfrac{2R_1^2R_2^2}{R_1^2+R_2^2}}$

These equations apply to both Newtonian and non-Newtonian flow. When the bitumens are made more fluid by increase of temperature, it is found that they tend to conform much more closely to ideal liquids. Viscosities may then be measured by a capillary U-tube viscometer, and the modified Ostwald instrument [9] designed primarily for tars and pitches has been found convenient, particularly for determining temperature coefficients.

## Some Experimental Results.

No bitumen so far examined has been found to possess a yield value, whatever the constant shear stress applied, and after sufficient time the

inner cylinder of the viscometer ultimately attains a constant angular rotation. When the load is removed the elasticity of the bitumen produces a recovery. A typical angular rotation-time curve is shown in Fig. 4, and indicates the four processes which operate during the flow of the material. The small initial curved portion *AB* arises from elastic elongation of the bitumen as well as from some viscous flow, and is related to the final elastic recovery. With fluid binders this elastic fore-effect occupies only a few seconds of time and is scarcely noticeable, but with harder

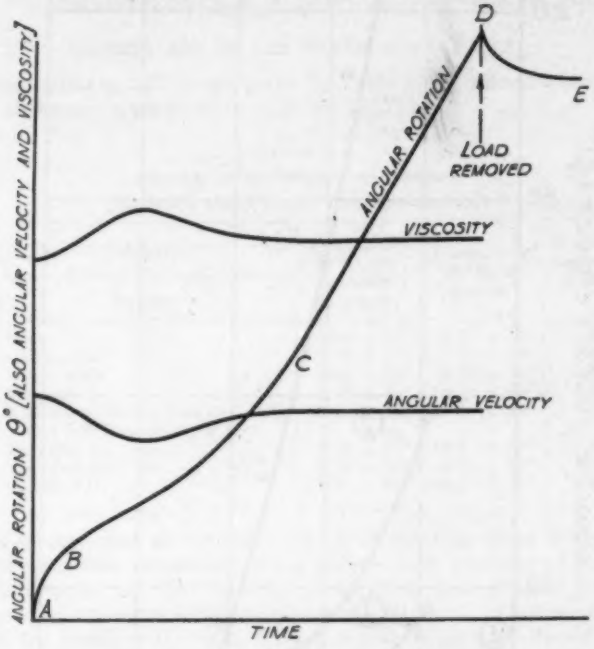



FIG. 4.

TYPICAL ANGULAR ROTATION/TIME CURVES FOR BITUMEN UNDER CONSTANT SHEARING STRESS.

Section AB. Initial Elastic Fore-Effect.
„ BC. Thixotropic Region.
„ CD. Final Constant Angular Velocity Region.
„ DE. Elastic Recovery. [Exaggerated Angle Scale.]

binders it occurs for a rather longer time. The section *BC*, which indicates a reduction in viscosity with continued working, is associated with thixotropy or the internal structure of the material. When the structure has been broken down to an equilibrium state corresponding to the stress applied, the curve straightens out (*CD*). It is from this portion of the curve (*i.e.*, where the angular velocity is constant) that the viscosity (applied stress/rate of strain) is calculated for the particular shearing stress applied. The elastic recovery, after removal of the applied stress, is

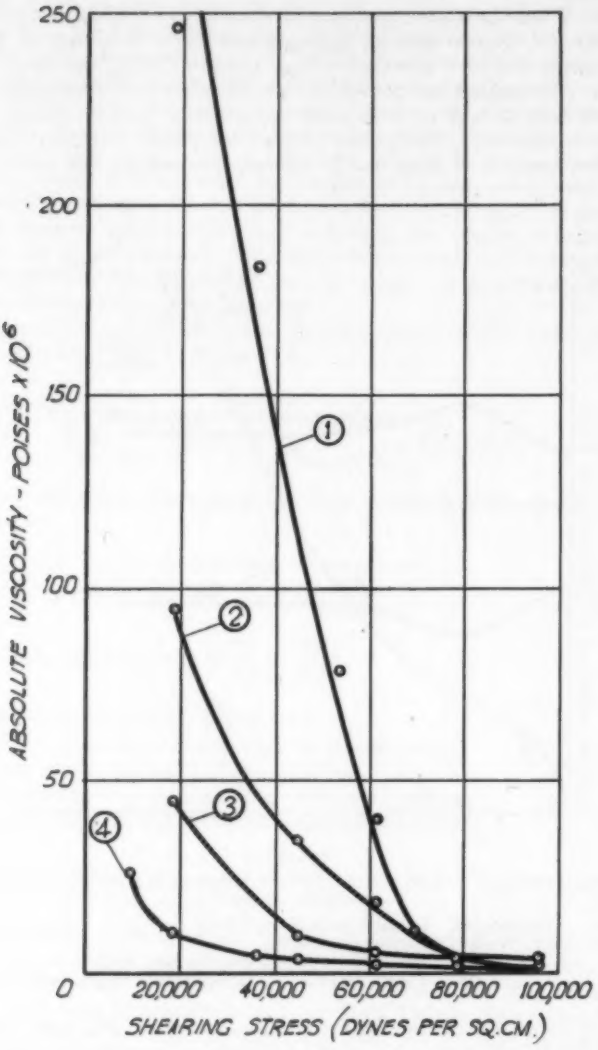



FIG. 5.

EFFECT OF SHEARING STRESS ON VISCOSITY OF E, AIR-BLOWN BITUMEN, AT DIFFERENT TEMPERATURES.

(1) Temperature 30·7° C.
(2) Temperature 40·2° C.
(3) Temperature 44·9° C.
(4) Temperature 49·2° C.

represented by *DE*. The corresponding angular velocities and apparent viscosities are also shown.

The viscosity of each material has been determined over a range of shearing stresses and temperatures. As previously stated, the viscosities vary with the shearing stress. An extreme case is shown in Fig. 5, in which the viscosity of the blown Mexican bitumen, *E*, is plotted against the corresponding shear stress at four temperatures from 30° C. to 49° C. The other bitumens have shown variations of this type, but to a less degree; the Californian bitumen, *A*, shows the least variation with stress.

## Significance of the Penetration Value.

The viscosities at 25° C. are given in Table I for different bituminous binders all having a penetration of 65 (at 25° C.).

Table I.

*Viscosity of 65 Penetration Bitumens.*

(Measured with Ostwald type Viscometers.)

| Type of Bitumen. | | Viscosity at 25° C. (extrapolated) in poises. | Viscosity at 40° C. in poises. | Logarithmic temperature coefficient "$n$." |
|---|---|---|---|---|
| Code. | Source. | | | |
| D | Miri | $1{\cdot}28 \times 10^6$ | $3{\cdot}55 \times 10^4$ | 12·0 |
| A | Californian | $1{\cdot}70 \times 10^6$ | $4{\cdot}87 \times 10^4$ | 11·9 |
| B | Venezuelan | $2{\cdot}64 \times 10^6$ | $9{\cdot}12 \times 10^4$ | 11·2 |
| C | Mexican | $3{\cdot}92 \times 10^6$ | $14{\cdot}3 \times 10^4$ | 11·1 |
| F | Mixture of Blown Mexican 44% and 200 Pen. Mexican 56% | $22{\cdot}1 \times 10^6$ | $57{\cdot}9 \times 10^4$ | 12·2 |
| H | Trinidad A.C. 5A | $4{\cdot}66 \times 10^6$ | $15{\cdot}9 \times 10^4$ | 11·3 |
| I | Trinidad A.C. 5B | $2{\cdot}78 \times 10^6$ | $8{\cdot}91 \times 10^4$ | 11·5 |
| J | Cuban A.C. | $44{\cdot}7 \times 10^6$ | $84{\cdot}1 \times 10^4$ | 13·3 |

It will be seen that at the particular mean shearing stress in the viscometers the extreme materials show a difference in viscosity of 35 times. These differences indicate that the penetration measurement has little significance as a measure of the viscosity of a bitumen. The precise depth to which the needle will sink in 5 seconds will be greatly affected by the degree of non-Newtonian flow, and will also depend on the thixotropic, elastic, and adhesive properties. With this instrument the effect of these properties is exaggerated in relation to that of the viscosity, and with some bitumens will have a predominating influence on the measurement. Further, besides the large change in stress which occurs during a measurement, a low-penetration bitumen is tested under much higher stresses than a high-penetration bitumen. The penetration test may therefore be quite misleading if it is used alone for comparing one bituminous material with another.

## Plastic Properties.

It is found that for most bitumens the relation between $D$ (rate of shear) and $S$ (shearing stress) may be expressed by the empirical equation

$$D = \frac{1}{\eta} S^P \quad . \quad . \quad . \quad . \quad . \quad (1)$$

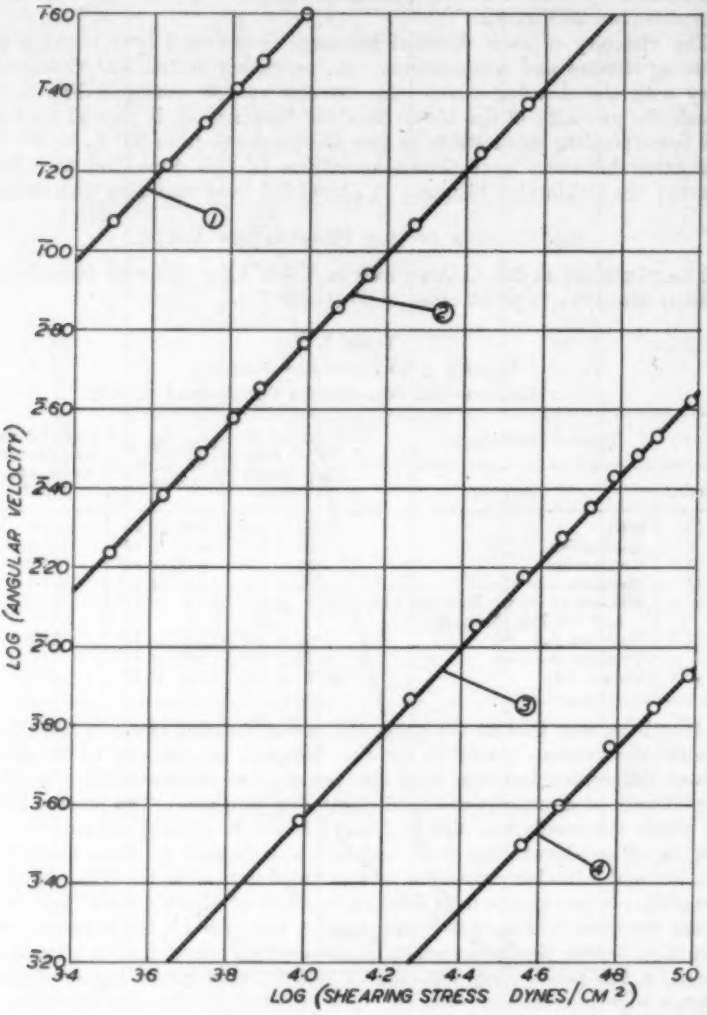



Fig. 6.

RELATION BETWEEN ANGULAR VELOCITY AND SHEARING STRESS FOR I, TRINIDAD ASPHALT 5B, AT DIFFERENT TEMPERATURES.

The results from the "plastic" air-blown bitumen, however, do not fit even this equation.

Fig. 6 shows the straight-line relation obtained on plotting log. angular velocity against log. shearing stress for the Trinidad A.C. 5B (I), at temperatures from 24° to 56° C. The slope of the lines gives the value of the index $p$. Other writers [10] have referred to the deviation from ideal flow exhibited by bituminous materials, but no method based on fundamental considerations has yet been proposed for defining the degree of plasticity. The "penetration index" used by Pfeiffer and Van Doormal [11]

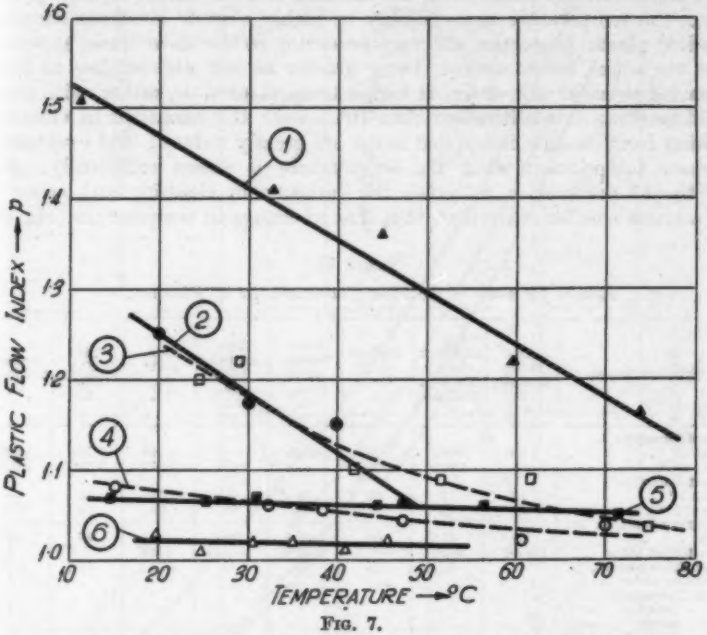



FIG. 7.

EFFECT OF TEMPERATURE ON PLASTIC FLOW INDEX OF 65 PENETRATION BITUMENS.

1. Mixture of Blown Mexican and Spramex. F.
2. Mexican. C.
3. Trinidad A.C. 5A. H.
4. Venezuelan. B.
5. Trinidad A.C. 5B. I.
6. Californian. A.

is largely determined by the plastic properties of the material. The use of the index $p$ in the above equation as a "plastic flow index" provides for the time being a method, based on the fundamental flow properties, of expressing the degree of plasticity where this is considered as the divergence from ideal viscous flow. The values of $p$ for the different materials are given in Table II, which contains other data on these materials.

As noted by previous writers, the deviation from ideal flow decreases as the materials are made more fluid by rise of temperature. The effect of temperature on the plastic flow index of the materials is shown in Fig. 7.

## Effect of Temperature on Viscosity.

All bituminous materials are characterized by the very large changes in viscosity produced by changes in temperature; this property is of vital importance in the use of the materials.

The curves given in Fig. 5 show values of the viscosity of *E*, the blown bitumen, obtained for a range of shearing stresses at temperatures between 30° and 49° C. The change in viscosity produced by this change in temperature is large when the shearing stress is 20,000 dynes/sq. cm., and comparatively small when the shearing stress is 80,000 dynes/sq. cm. Thus the temperature susceptibility of highly viscous bitumens showing marked plastic properties will vary according to the shear stress at which the viscosities are measured, being greater at low and smaller at high shearing stresses. However, at higher temperatures, or, rather, with more fluid products (viscosities less than $10^4$ poises), the variations in viscosity arising from changes in applied stress are greatly reduced, and eventually become insignificant when the temperature is raised sufficiently. For all the 65 penetration materials the variation in viscosity with stress is of a much smaller order than that due to change in temperature (Fig. 9).

Table II.

*Results for some of the Flow Characteristics of Bitumen.*

| Type of bitumen. | Air-blown Mexican, E. | 44% air-blown 56% 200 Pen. Mexican, F. | Mexican 60/70 Pen., C. | Venezuelan 60/70 Pen., B. | Californian 60/70 Pen., A. | Trin. A.C.* 5A, H. | Trin. A.C.† 5B, I. | Mexican 200 Pen., G. |
|---|---|---|---|---|---|---|---|---|
| Specific gravity :— | | | | | | | | |
| At 15° C. . . | 1·051 | 1·042 | 1·045 | 1·025 | — | 1·244 | 1·164 | 1·035 |
| At 25° C. . . | — | 1·028 | 1·039 | — | 1·015 | 1·237 | 1·152 | 1·025 |
| Penetrations :— | | | | | | | | |
| At 15° C. . . | 13 | 29 | 26 | 26 | — | 24 | 28 | — |
| At 25° C. . . | 22 | 60 | 63 | 64 | 66 | 59 | 66 | 199 |
| Softening point, R. and B. . . . . | 85·5 | 57·2 | 52 | 49·7 | 45·6 | 51·1 | 66 | 40 |
| Penetration index . | +3·2 | +1·2 | −0·1 | −0·6 | −1·75 | −0·5 | −1·5 | 0 |
| Asphaltene content, %. | 37 | 27 | 20 | 13 | 4 | 21‡ | 15‡ | 17·7 |
| Viscosity at 25° C. :— | | | | | | | | |
| (a) Determined in Ostwald viscometer mean stress about 3,000 dynes/sq. cm. . | — | $22·1\times10^6$ | $3·22\times10^6$ | $2·64\times10^6$ | $1·70\times10^6$ | $4·66\times10^6$ | $2·78\times10^6$ | $2·98\times10^6$ |
| (b) Determined in Concylindric viscometer mean stress 36,130 dynes/sq. cm. . | $3·0\times10^5$ | $5·64\times10^5$ | $3·47\times10^5$ | $2·11\times10^5$ | $1·91\times10^5$ | $3·65\times10^5$ | $1·94\times10^5$ | $2·32\times10^5$ |
| Log temperature coefficient . . . | — | 11·1 | 11·4 | 11·6 | 11·8 | 11·0 | 10·6 | 9·7 |
| Plastic flow index ($p$) at 25° C. . . . | 3 | 1·44 | 1·22 | 1·10 | 1·02 | 1·2 | 1·08 | 1·19 |
| Maximum elastic recovery, degrees in Couette viscometer at 25° C. . . . | 8 | 5 | 4 | 2 | 0·5 | 1 | 1 | 3·7 |

* Trinidad A.C. 5A consists of 83·5% of Trinidad Epure and 16·5% of Flux Oil.
† Trinidad A.C. 5B consists of 49·5% of Trinidad Epure, 5% of Flux Oil, 45·5% 200 pen. Venezuelan Bitumen.
‡ Estimated on the extracted bitumen.

Fig. 8 shows the values of log. viscosity over a temperature range from 25° C. to 90° C. for six bitumens (each having a penetration of 65 at 25° C.)

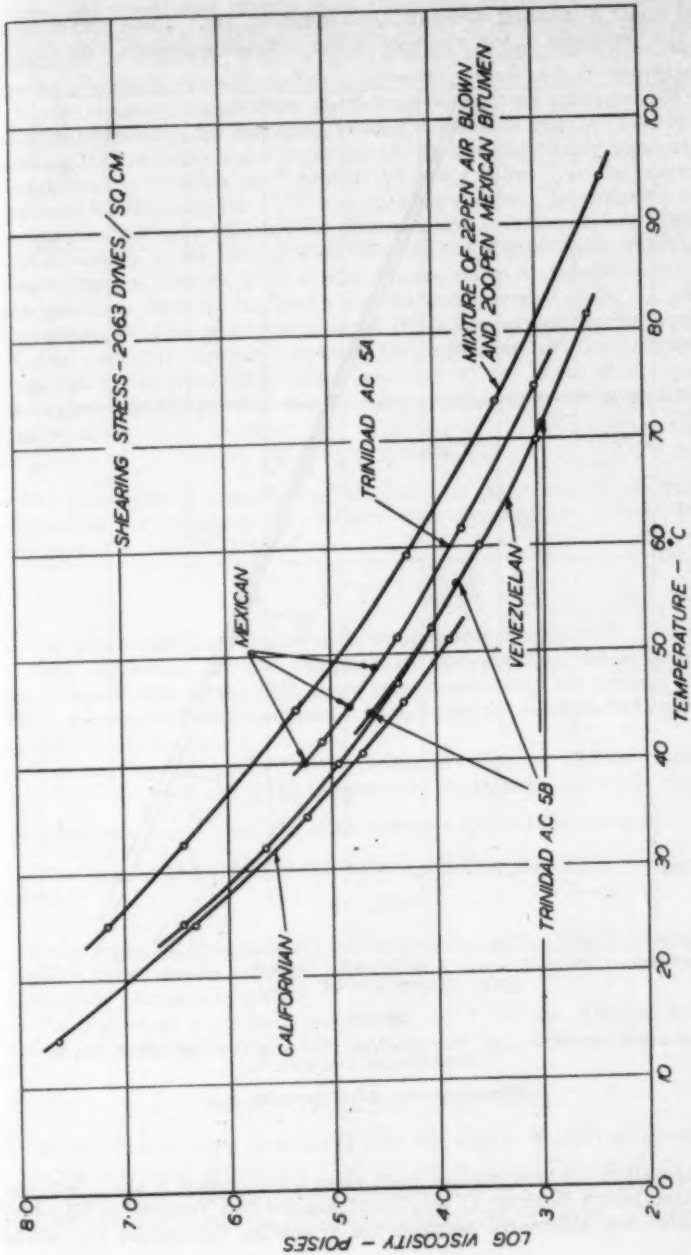



FIG. 8.

EFFECT OF TEMPERATURE ON LOG. VISCOSITY OF BITUMENS (65 PENETRATION).

tested under a shearing stress of 2,063 dynes/sq. cm. These curves show that the variations in log. viscosity of the different materials with change

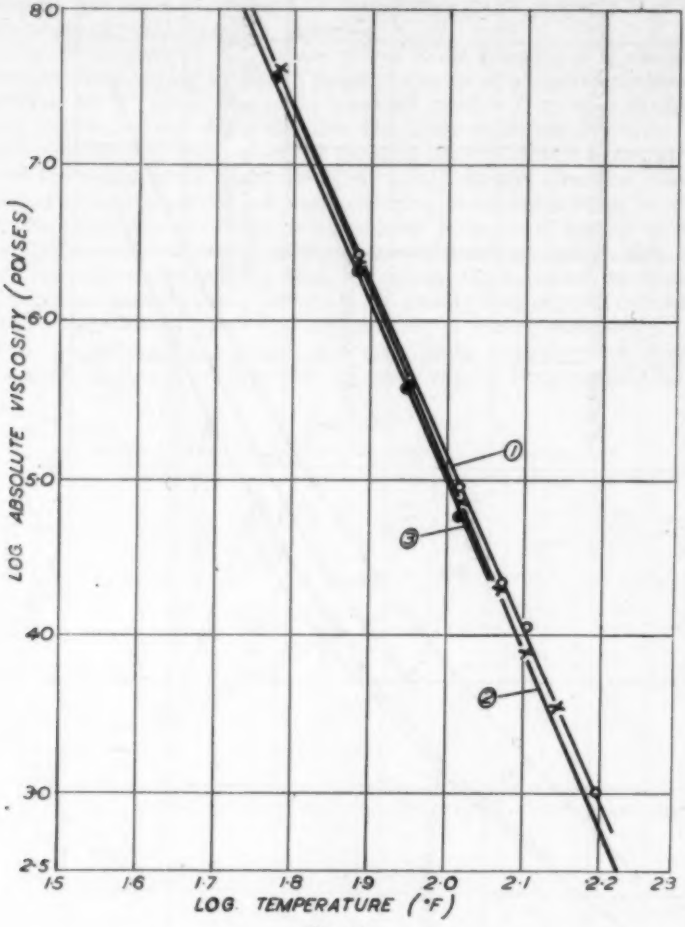



FIG. 9.

RELATION BETWEEN LOG. TEMPERATURE (°F.) AND LOG. VISCOSITY FOR B, VENEZUELAN BITUMEN.

1. Shearing stress 2,063 dynes/sq. cm.
2. ,, ,, 9,730 ,, ,,
3. ,, ,, 36,130 ,, ,,

of temperature are very similar, even when a comparison is made between the fluxed blown Mexican, C, and the steam-distilled Venezuelan bitumen, B. There are differences between the viscosities throughout the whole

range, but these arise mainly from the initial differences in viscosity at 25° C. Curves of this type provide no means of defining the temperature coefficient of viscosity, since a given change in temperature produces a greater change in viscosity at low temperatures than at high temperatures. Various viscosity/temperature coefficients have been proposed for bituminous materials; for example, Traxler [12] assumes that the curved lines relating log. viscosity and temperature (° C.) are sufficiently straight over a small range to define an "Asphalt Viscosity Index" as the percentage decrease in viscosity for 1° C. rise in temperature. In order to obtain a single numerical coefficient for extrapolation and comparison purposes, it is necessary to use functions of viscosity and temperature which give a linear relation over as large a temperature range as possible. Accurate straight lines have so far been obtained over a range of 70° C. for any bituminous binders up to viscosities of $10^7$ poises on plotting the logarithm of the apparent viscosity against the logarithm of the temperature Fahrenheit, the viscosities being measured at the same shearing stress throughout the temperature range; some typical curves are given in Fig. 9. The equation

$$\log.\ \eta = a - n \log.\ T,$$

which also holds for coal-tars and pitches, thus provides a simple empirical expression for variation of viscosity with temperature defined by one constant, viz. :—

$$n = \frac{\log.\ \eta_1 - \log.\ \eta_2}{\log.\ T_2 - \log.\ T_1} \quad . \quad . \quad . \quad . \quad (2)$$

$n$ has been called the "logarithmic temperature coefficient."

This expression for the temperature susceptibility, while inaccurate for extrapolation to the high temperatures necessary for mixing, is valid for a temperature range sufficient to indicate the relative susceptibilities of different bitumens.

The equation $\eta = aT^{-n}$ is a particular case of Slottes' formula [13] $\eta = C/(b + t)^n$, where $t$ is the temperature Centigrade, and where the value of $b$ becomes $\frac{5 \times 32}{9}$ and the other contents are suitably chosen.

The theoretical formula of Andrade [14] and Sheppard [15]

$$\eta = Ae^{-k/\theta}$$

where $\theta$ is absolute temperature, which was derived for pure monomolecular liquids, would not be expected to hold for the complicated mixtures which constitute bitumens and tars.

The values of $n$ in the equation $\eta = aT^{-n}$ for the different bitumens are given in Table II.

## Elastic Properties of Bitumens.

It has already been mentioned that the elastic or solid properties of a bitumen are most prominent when the stress is rapidly applied or varied, but, even when a bitumen has been sheared slowly under constant stress, elastic recovery occurs on the sudden removal of the stress. The amount

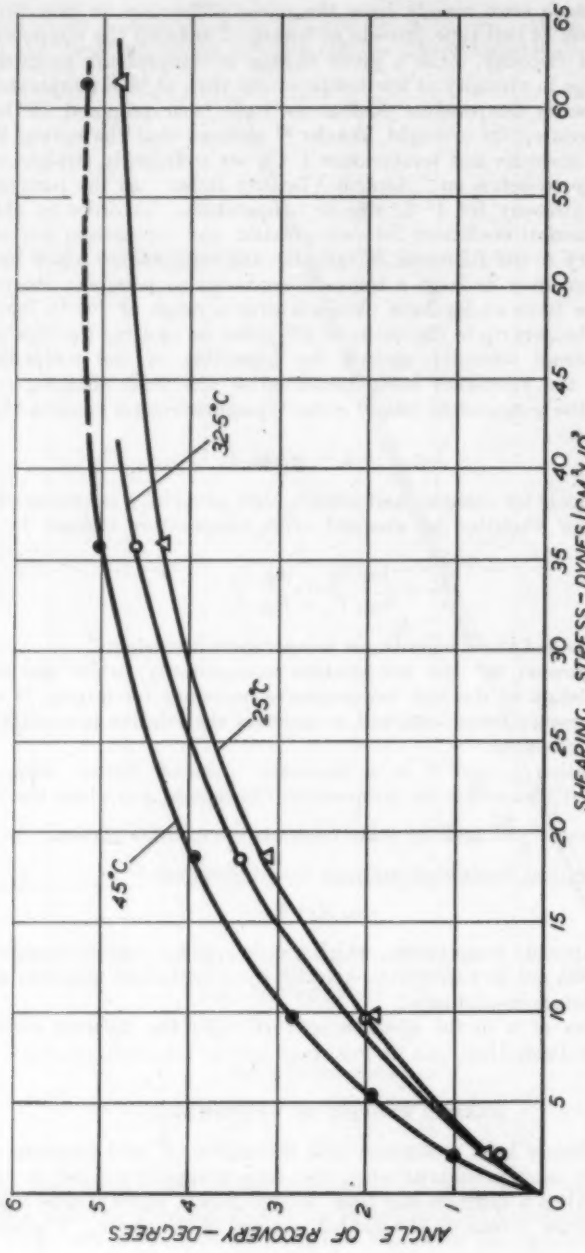



FIG. 10.

RELATION BETWEEN SHEARING STRESS AND TOTAL ELASTIC RECOVERY OF F, 65 PENETRATION MIXTURE OF BLOWN AND 200 PENETRATION MEXICAN BITUMEN.

of recovery depends on the stress applied and the degree to which the material has been previously sheared. For a given stress, the recovery increases to a definite maximum value with increase in the previous shear. Fig. 10 shows the relation between the applied stress and the maximum recovery for the fluxed blown bitumen, *F* (65 pen.).

From the angular recovery values which occur on the removal of definite applied stresses an apparent rigidity modulus, taken as the ratio of shear stress to shear recovery, has been calculated for various values of the shearing stress. Allowing for the dimensions of the viscometer and assuming that the recovery corresponds to a simple shear motion with no flow, the shear recovery is equal to five times the measured angular recovery ($\alpha$) of the inner cylinder. These calculated values are tabulated in Table III.

TABLE III.

*Apparent Moduli of Rigidity for Fluxed Blown Bitumen F.*

| Temperature. | Shearing stress (dynes/sq. cm.) S. | Angle of recovery (degrees) a. | Apparent modulus of rigidity (dynes/sq. cm.) S/5a. |
|---|---|---|---|
| 25° C. | $1{\cdot}5 \times 10^3$ | 0·4 | $4{\cdot}3 \times 10^4$ |
| ,, | $10{\cdot}0 \times 10^3$ | 2·0 | $5{\cdot}7 \times 10^4$ |
| ,, | $17{\cdot}5 \times 10^3$ | 3·0 | $6{\cdot}8 \times 10^4$ |
| ,, | $30{\cdot}0 \times 10^3$ | 4·0 | $8{\cdot}6 \times 10^4$ |
| ,, | $47{\cdot}5 \times 10^3$ | 4·6 | $11{\cdot}9 \times 10^4$ |
| 45° C. | $2{\cdot}5 \times 10^3$ | 1·15 | $2{\cdot}5 \times 10^4$ |
| ,, | $5{\cdot}0 \times 10^3$ | 1·87 | $3{\cdot}05 \times 10^4$ |
| ,, | $10{\cdot}0 \times 10^3$ | 2·85 | $4{\cdot}0 \times 10^4$ |
| ,, | $20{\cdot}0 \times 10^3$ | 4·02 | $5{\cdot}4 \times 10^4$ |
| ,, | $35{\cdot}0 \times 10^3$ | 4·96 | $8{\cdot}0 \times 10^4$ |

Fig. 10 shows that for the 65 penetration fluxed blown bitumen, *F*, a change of temperature from 25° to 45° C. produces little change in the elastic recovery. It has been found that for the bitumens investigated there is a temperature range within which the recovery is a maximum; above and below this range the recovery diminishes, and at high temperatures, at which the materials are quite fluid, the elastic recovery eventually disappears. Over the range of temperature from 25° to 45° C. the change in the apparent rigidity modulus of the bitumen is of a much lower order than the change in viscosity. As would be expected from consideration of viscous internal damping, the rate of recovery increases as the temperature of the bitumen is raised or its viscosity reduced. The values for the apparent rigidity modulus (2 to 12 $\times 10^4$ dynes/sq. cm.) are of a lower order than values of the rigidity modulus of bitumen obtained by dynamic methods (*e.g.*, Lonsdale and Wilson,[16] $10^8$ dynes/sq. cm.).

## COMPARISON OF BITUMENS.

The results given in Table II show that the bitumens so far investigated differ chiefly in their plastic and elastic properties, and the temperature differences found necessary in practice in the use of the materials appear

to be due primarily to differences in these properties, and to the difference in initial viscosity of the bitumens arising from the adoption of a standard penetration to which the various materials must conform.

There is little difference between the logarithmic temperature coefficients of viscosity, although the Californian bitumen, *A*, has the highest coefficient, and the blown bitumen, *F*, the least. These facts are substantially in agreement with the conclusions of Pfeiffer and Van Doormal (*loc. cit.*), and the explanation put forward by these authors to account for the differences in rheological properties of different types of bitumen are so far supported by the present results.

## Rheology of Asphaltic Road Mixtures.

The flow properties of a bitumen-aggregate mixture are directly influenced by the flow properties of the bituminous binder. The large

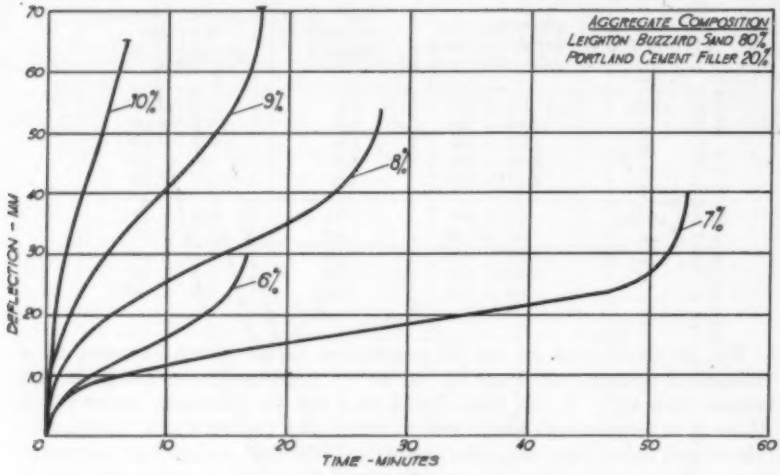



Fig. 11.

EFFECT OF BINDER CONTENT ON THE DEFLECTION OF BEAMS OF SAND ASPHALT.

Storage time 8 days. Temperature of test 25° C. Dimensions of beams 10″ × 2″ × 1″.
Binder—Trinidad Asphaltic Cement—Type 5A. Percentage of Soluble Bitumen Marked on Curves.

amount of work on measuring the mechanical properties of such mixtures [17] done by earlier investigators is, on examination, usually found to comprise the measurement of flow properties under various arbitrary conditions of stress.

Among a considerable number of tests investigated those selected for the present purpose are the beam and tensile tests. The methods and technique adopted for preparing and testing specimens have been described elsewhere.[18, 19] Although for certain purposes the two tests give the

same information, the tensile test has the advantage that the results may be expressed quantitatively, are independent of the dimensions of the specimen, and that the material is subjected to a constant uniform stress or rate of strain. The experimental procedure has been to obtain the deformation-time curves given by roller-compacted rectangular specimens. Two fundamental characteristics are thus obtained—namely, the rate of flow under a known stress and the extensibility or total flow before failure. Information on the flow properties of the mixtures involves a study of the variations of these quantities with stress, temperature, and age.

Some typical deformation-time curves are shown in Fig. 11. The resulting deformation of the tensile specimen may be considered as due to two shear stresses of one-third the tensile stress.[20] The rate of elongation may be shown to be equal to the rate of shear strain.

The ratio of the stress to the slope of the straight-line portion of the curves (the minimum rate of deformation) may be considered a measure of the viscosity of the material. On this basis, from the curves shown in Fig. 11, the specimen containing 7 per cent. of bitumen exhibits the maximum resistance to deformation, and from this point of view 7 per cent. may be considered the optimum binder content for the particular aggregate. This optimum binder content has been determined for each bitumen-aggregate mixture referred to below.

### Effect of Stress on Rate of Strain.

In Fig. 12 some typical stress–rate of strain curves are shown for specimens of sand asphalt, each made with its optimum binder content. When, from such results, log. stress is plotted against log. minimum rate of strain, straight lines are obtained, as shown in Fig. 13. Thus these results show that the relation between stress and minimum rate of strain may be expressed by the equation

$$R = KS^P \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $R$ is the minimum rate of strain,
$S$ is the applied stress,
$K$ and $P$ are constants.

In Fig. 13 the slope of the straight lines is constant over the temperature range investigated. $P$ may thus be considered to be a characteristic of the material representing the divergence of the flow from that expressed by a linear relation between stress and rate of flow. By analogy with the equation applicable to bitumens, $P$ may therefore be termed the "plastic flow index" of the bitumen-aggregate mixture. The value of the constant $K$ in the above equation represents the minimum rate of deformation at unit stress, and is thus a measure of the "mobility" of the material (*i.e.*, rate of flow/unit stress).

### Effect of Temperature on Rate of Strain.

It has been found that a straight-line relation exists between log. $K$ and temperature over a temperature range of about 25° C.; Fig. 14 shows

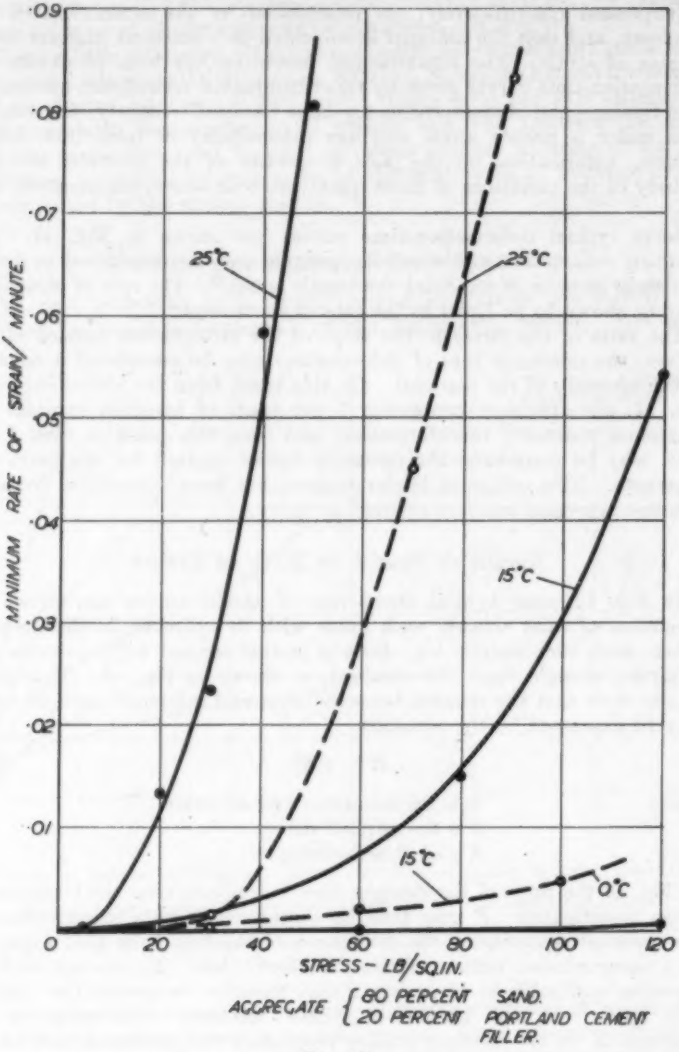



FIG. 12.

RELATION BETWEEN STRESS AND RATE OF STRAIN FOR SAND ASPHALTS AT VARIOUS TEMPERATURES.

— — — Laboratory Prepared Material containing Venezuelan Bitumen.
——— Material from Public Road.

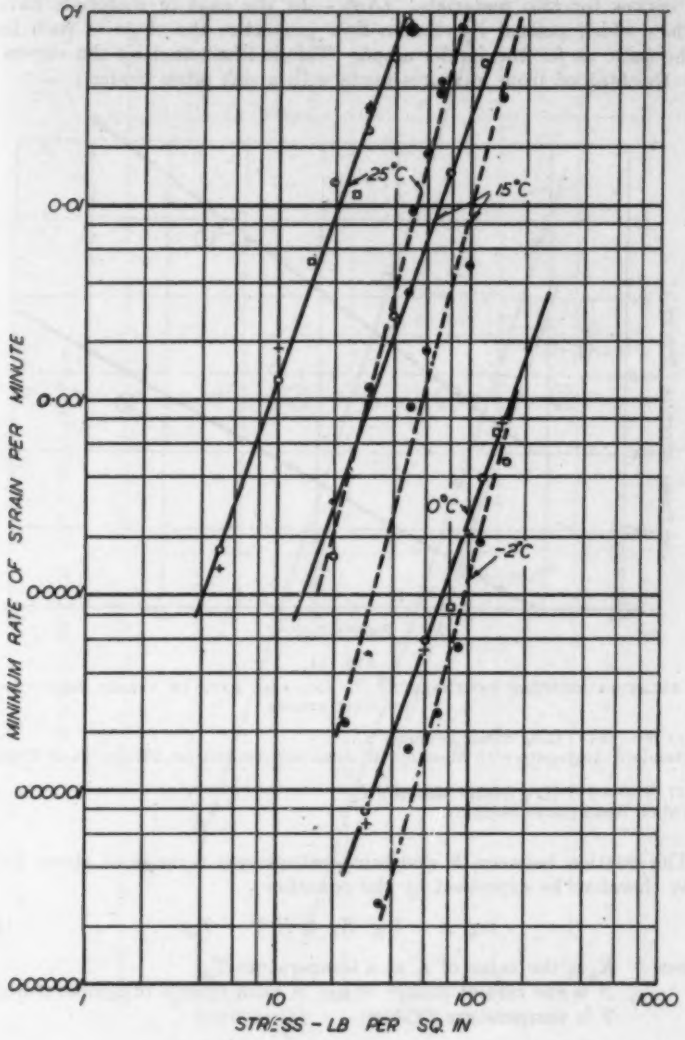



Fig. 13.

RELATION BETWEEN LOG. STRESS AND LOG. MINIMUM RATE OF STRAIN OF SAND ASPHALT AT VARIOUS TEMPERATURES.

the curves for two materials. (*Note.*—In the case of materials having binders which possess Newtonian flow properties the slope of such lines is the same as for the binder alone. This is illustrated by the curves in Fig. 15 obtained from mixtures made with a soft pitch binder.)

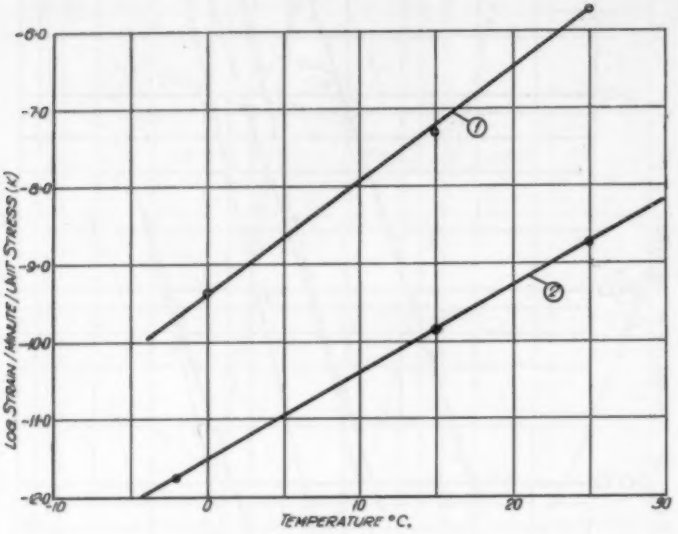



FIG. 14.

RELATION BETWEEN TEMPERATURE °C. AND LOG. RATE OF STRAIN PRODUCED BY UNIT STRESS

(1) $N = 0{\cdot}147$ (Log Strain/Minute)/°C.
Standard Aggregate with Mexican Bitumen and Venezuelan Bitumen and Trinidad 5A.
(2) $N = 0{\cdot}111$ (Log Strain/Minute)/°C.
Public Road (Good Section).

The relation between $K$ and temperature over a range of about 25° C. may therefore be expressed by the equation

$$\log. K = \log. K_0 + N(T - T_0) \quad . \quad . \quad . \quad (4)$$

where $K_0$ is the value of $K$ at a temperature $T_0$,
$N$ is the rate of change of log. $K$ with change of temperature,
$T$ is temperature (°C.).

Equation (3) may therefore be written

$$\log. R = P \log. S + \log. K_0 + N(T - T_0).$$

Thus, over a range of temperature of about 25° C. the flow properties at the minimum rate of deformation of a bitumen-aggregate mixture under conditions of constant tensile stress may be expressed by the constants $P$, $K_0$, $N$, and the extensibility or percentage strain at failure.

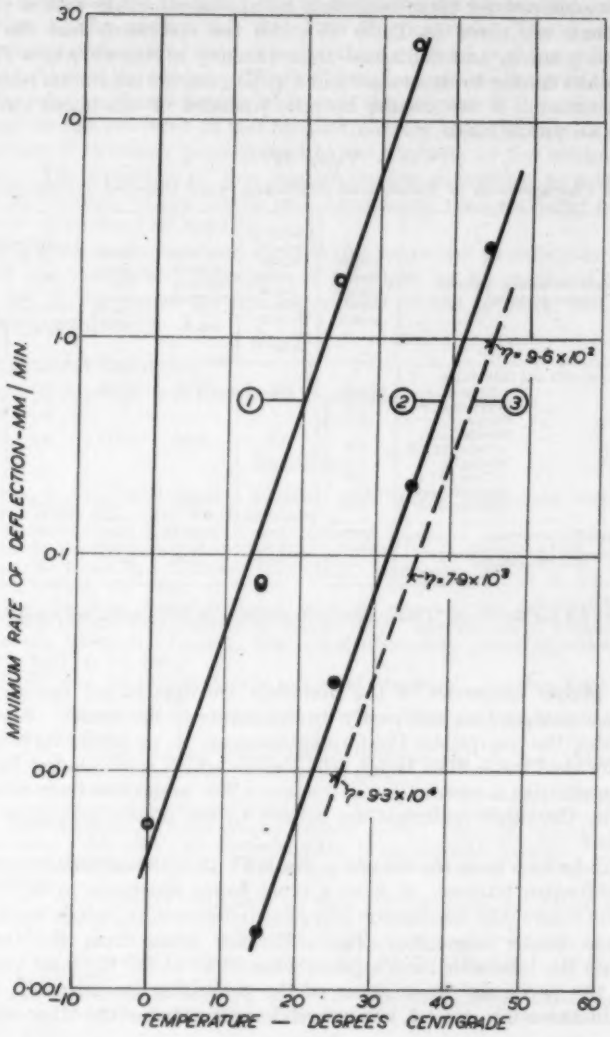



FIG. 15.

EFFECT OF TEMPERATURE ON MINIMUM RATE OF DEFLECTION OF BEAMS AND ON VISCOSITY $\eta$ OF BINDER.

(1) Sand 80%, Portland Cement 20% } 10% Binder.
(2) Sand 60%, Limestone Dust 40% } 11% Binder.
(3) Temperature Fluidity Line for the 300 Pen. Pitch Binder.

Values obtained for these constants for specimens made with a variety of bitumens are given in Table IV. All the specimens had the same aggregate grading, and contained that quantity of binder which from a set of results similar to those shown in Fig. 10 gave the maximum resistance to deformation. A few results are also included of specimens cut from asphalts on public roads.

TABLE IV.

*Flow Characteristics of Bituminous Specimens under Constant Tensile Stress.*

| Specimens containing optimum binder contents. | Soluble bitumen content (per cent.). | Change of rate of strain with stress (plastic flow index), $P$, at 25° C. | Log. rate of strain for unit stress at 0° C., log.$K$. | Change of log.$K$ with temperature, $N$. | Extensibility, 50 lb./sq. in. $E$. | |
|---|---|---|---|---|---|---|
| | | | | | 25° C. | 0° C. |
| Standard Aggregate and Californian Bitumen A | 7·5 | 2·0 | −8·35 | 0·170 | 8·7 | 7·3 |
| " " " Venezuelan B | 7·5 | | | | 6·1 | 6·0 |
| " " " Mexican C | 8·0 | | | | 7·1 | 6·2 |
| " " " Trinidad A.C. (Type 5A) H | 7·0 | 2·8 | −9·34 | 0·147 | 3·6 | 3·1 * |
| " " " Trinidad A.C. (Type 5B) I | 7·0 | | | | — | — |
| " " " Blown Mexican and Spramex, F | 8·75 | 3·2 | −9·42 | 0·115 | 10·0 | 7·0 |
| †Public Road No. 2—Good | 10·25 | 3·91 | −11·78‡ | 0·111 | 4·0 | 1·5 ‡ |
| † " " No. 12—Cracked | 8·70 | 3·95 | −13·95 | 0·137 | 2·0 | 0·5 § |
| " " No. 22—Cracked | — | 5·28 | −16·25 | 0·129 | 1·1 | 0·15 § |

* At 100 lb./sq. in.
† Roads No. 2 and No. 12 were 13 years old and both contained the same bitumen and aggregate.
‡ At −2° C.
§ At 150 lb./sq. in.

The plastic properties of the materials are determined partly by the aggregate composition and partly by the nature of the binder. Specimens containing the non-plastic Californian bitumen, *A*, as binder have a value of 2·0 for the Plastic Flow Index ($P$), a value which is also found for specimens containing a viscous tar as binder. The variations from this value given by the other materials are related to the plastic properties of the bitumens.

It will be seen from the results in Table IV that the materials containing the Californian bitumen, *A*, have a much lower resistance to deformation than the others (the comparison being made between materials having their optimum binder contents). This difference arises from the fact that although the bitumens have a penetration of 65 at 25° C., their viscosities under the particular shear stress of the test differ considerably, that of the Californian bitumen, *A*, being much less than that of the other bitumens.

## CONCLUSIONS.

The examples given in this paper of the results of the investigation of the fundamental flow properties of bituminous materials illustrate the progress made in understanding the problems.

The flow properties of a bitumen-aggregate mixture are determined by the nature and grading of the aggregate and by the quantity, the viscosity,

and the nature of the binder. The more plastic the binder, the greater is the value of the plastic flow index of the mixture. The logarithmic temperature coefficient of flow of the mixture (defined as $\Delta \log. r/\Delta \log. T$) is equal to that of the binder. The fact that, for a given change in temperature, the relative change in rate of flow of the mixture is the same as that produced in the viscosity of the binder indicates that the rate of flow of the mixture is inversely proportional to the viscosity of the binder in the mixture. The existence of this relation makes it possible to follow the change in viscosity of the binder in a bituminous road-surfacing material by means of mechanical tests.

Further work on the lines described in this paper will provide information enabling the mechanical properties of mixtures to be predicted from a knowledge of the properties and proportions of the bitumen and of the aggregate constituents.

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# THE SYNTHESIS OF LUBRICATING OILS BY CONDENSATION REACTIONS.*

## PART I.—THE CONDENSATION OF CHLORINATED PARAFFIN WAX WITH AROMATIC HYDROCARBONS.

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High-boiling hydrocarbons were synthesized by Friedel and Crafts in their investigations on the reaction of alkyl halides with aromatic hydrocarbons using aluminium chloride as catalyst.

This classical reaction opened a new field for the synthesis of hydrocarbons and has been used and developed extensively; but only recently has this condensation type of reaction been utilized for the production of viscous hydrocarbons of high boiling point and possessing good lubricating properties.

The Friedel–Crafts condensation has been used by Fischer [2, 3] for the production of lubricating oils from the liquid products, designated by the term "Kogasin," synthesized from water-gas by low-pressure catalysts. The fraction boiling above 220° C., essentially paraffinic in character, was chlorinated at room temperature. The chlorinated material was then mixed with aromatic hydrocarbon and anhydrous aluminium chloride, and the reaction, which commenced at room temperature, completed by heating on a water-bath. The products separated from the aluminium chloride sludge were refined with bleaching earth and vacuum distilled, the refined products varying from medium to highly viscous oils. In addition, Fischer has investigated the dechlorination of the chlorinated Kogasin in the presence of activated aluminium (aluminium mercury couple). In the preparation of the pour-point depressant "Paraflow" chlorinated paraffin wax is condensed with an aromatic hydrocarbon in the presence of aluminium chloride.

The manufacture of pour-point depressants by the condensation of chlorinated paraffin wax with cyclic hydrocarbons [5] and with hydroxy compounds [5] using an aluminium chloride catalyst has been proposed. Products, used as pour point, viscosity index, and colour improvers, have been claimed [7] by the condensation of chlorinated paraffin wax with aromatic hydrocarbons using as catalyst aluminium chloride, together with a metal chloride of the first or second groups of the periodic table. The manufacture of addition agents for improving oiliness [8] and the manufacture of lubricating oils [9] by condensing aromatics with chlorinated paraffin wax have also been suggested.

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Preliminary experiments on the action of metallic aluminium on chlorinated hydrocarbons indicated that:

1. Chlorinated hydrocarbons undergo a reaction, apparently of the Friedel–Crafts type, when heated in the presence of metallic aluminium.
2. Alkyl chlorides such as amyl chloride yield viscous oils, apparently of unsaturated character.
3. Alkyl chlorides in the presence of aromatic hydrocarbons yield viscous oils.
4. Chlorinated naphthenes, such as chloro*cyclo*hexane, alone or in the presence of aromatic hydrocarbons, yield asphaltic and resinous materials.
5. Zinc also catalyses this reaction to a slight extent, but alumina and metallic tin do not induce any reaction.

From this preliminary work it was decided to investigate the synthesis of lubricating oils by the condensation of alkyl chlorides with aromatic hydrocarbons, using metallic aluminium as a catalyst.

Available data on the relationship between constitution and physical properties of hydrocarbons indicate that long paraffin chains are valuable components of lubricating oil molecules.[10, 11] For the synthesis of lubricants, therefore, it is desirable to use alkyl chlorides with long carbon chains, such compounds being conveniently prepared by the chlorination of solid paraffin hydrocarbons.

A Burmah paraffin wax, melting point 51° C., was therefore chlorinated to three chlorine contents: 10 per cent. chlorine content, corresponding analytically to monochloroparaffin; 17 per cent., corresponding analytically to dichloroparaffin, and 25 per cent., corresponding analytically to trichloroparaffin. Since chlorination does not proceed in simple and complete stages, these chlorinated waxes are probably mixtures of unchlorinated paraffins, mono-, di-, and higher chloroparaffins.

### Condensation of Chlorinated Paraffin Waxes with Aromatic Hydrocarbons.

Condensation reactions with chlorinated paraffins and aromatic hydrocarbons were carried out in 5-litre, three-necked pyrex flasks fitted with reflux condenser, glass stirrer, and thermometer. The outlet tube from the top of the reflux condenser was connected to a Dreschel wash-bottle and water-pump in order to remove conveniently the hydrogen chloride fumes which were evolved in large amount during the reaction. Preliminary experiments were carried out to ascertain the proportions of chloroparaffin, aromatic hydrocarbon, and aluminium catalyst required.

Experiments with chlorinated wax (25 per cent. chlorine content) and excess benzene showed that the chloroparaffin and benzene reacted in approximately molecular proportions. Experiments with an excess of aluminium catalyst indicated that 1·4–1·5 per cent. of aluminium metal, calculated on weight of chloroparaffin, was required in the reaction. In the final procedure 500 gm. chlorinated wax, 50 gm. aromatic hydrocarbon, and 10 gm. aluminium were used.

Difficulties were encountered in the working up of the reaction product,

owing to the formation of emulsions. In addition, the colour of the final product from the preliminary experiments varied from dark green to black. In the early experiments the reaction product was allowed to stand for several hours in order to settle out a lower layer of heavy sludge. The upper liquid layer was decanted, washed with water to decompose and remove aluminium chloro-complexes, then washed successively with dilute caustic soda, dilute sulphuric acid, and water. Each washing stage resulted in the formation of emulsions which were extremely persistent. In spite of repeated treatment with water, acid, and alkali, the colour of the final product was dark green or black, comparing unfavourably with refined mineral oils. This dark colour was traced to small amounts of the lower layer sludge, which remained in suspension in the upper layer. A prolonged settling period improved the colour of the final product, but centrifuging had eventually to be adopted to remove the last traces of heavy sludge. Further, it was found that percolation filtration of the water-washed product through a granular bleaching earth of the floridin type was sufficient refining treatment, replacing efficiently the alkali and acid washes, and yielding clear, light-coloured oils. The finally adopted and most satisfactory experimental procedure consisted of the following :—

In a three-necked reaction flask were placed 500 gm. chlorinated wax, 50 gm. aromatic hydrocarbon, 10 gm. aluminium metal fillings, and 500 c.c. diluent (petroleum ether or refined kerosine). The mixture was stirred vigorously and heated until the diluent was refluxing steadily. A preliminary induction period of 1–6 hr., according to the aromatic hydrocarbon used, was usual before the condensation reaction began. Evolution of large quantities of hydrogen chloride accompanied the reaction, and during its progress the liquid darkened in colour. In the initial stages of the reaction it was essential to control the temperature to prevent the reaction proceeding too vigorously. In the later stages the reaction was completed by heating gently with steady refluxing for 1–2 hr. until no further fumes of hydrogen chloride were evolved. The total time for the condensation reaction was 4–6 hr. The liquid product was then allowed to stand for some hours, during which two liquid layers were formed. The upper layer was decanted off and centrifuged to remove final traces of sludge. The liquid was then agitated vigorously with water until an emulsion was formed. This emulsion broke on standing for a short time, and complete separation of water was obtained by further centrifuging. This treatment was followed by percolation through a granular bleaching earth, which rendered the liquid light and clear in colour. Removal of petroleum-ether diluent was effected by distillation, and blowing with nitrogen to remove the last traces. The kerosine diluent, used when naphthalene was the aromatic constituent, required vacuum distillation up to 250° C./10 mm. for complete removal.

### Condensation of Aromatic Hydrocarbons with Chlorinated Paraffin Wax of 10 per cent. Chlorine Content.

*Experiment A/W 40.*

A chlorinated wax with 10 per cent. chlorine content, corresponding analytically to monochloroparaffin, was condensed with benzene, by the

procedure described above. The diluent used was petroleum ether, b.pt. 100–120° C., and a trace of iodine (5–10 mg.) was added as a promoter. The reaction was initiated by refluxing at 110° C. for approximately 2 hr., and was completed by heating gently for 6 hr. The product was a white, waxy solid at room temperature with a pour point of 85° F., and above this temperature a pale mobile oil.

*Experiment A/W* 37.

A similar procedure was employed, with toluene as the aromatic component. The reaction commenced after a short induction period of 1 hr. The product was a yellowish-white, waxy solid at room temperature with a pour point of 85° F.

*Experiment A/W* 38.

In a third experiment naphthalene was used as the aromatic constituent. Naphthalene reacts less readily, higher temperatures—150–200° C.—being necessary to initiate the reaction. Kerosine was therefore used as diluent. The kerosine was rendered inert by refining with several batches of concentrated sulphuric acid, followed by alkali-washing, water-washing, and distillation. There was a prolonged induction period before the condensation reaction commenced. The reaction product was settled, centrifuged, water-washed, and filtered through bleaching earth. The kerosine diluent was removed by vacuum distillation, three fractions being obtained. The first fraction, distilling up to 190° C./30 mm., consisted of kerosine, the fraction distilling between 190° C./30 mm. and 200° C./10 mm. consisted of kerosine and white wax, and the residual fraction was a viscous oil with blue fluorescence and a high pour point (85° F.).

The dark colour of the naphthalene product is probably due to slight decomposition of the chloroparaffins during the induction period.

*Experiment A/W* 36.

For comparison an ordinary Friedel–Crafts condensation was carried out using the 10 per cent. chlorinated wax and toluene with 10 per cent. anhydrous aluminium chloride as catalyst in place of the aluminium. With this reactive catalyst the condensation proceeds at room temperature. The product was a whitish-yellow waxy solid at room temperature with a pour point of 85° F.

## Properties of Condensation Oils.

The properties of the condensation product of toluene and chlorinated wax of 10 per cent. chlorine content are compared with those of two commercial oils of similar specific gravity in Table I.

The laboratory inspection data for the condensation product compare favourably with those for the commercial oils.

The product has a low viscosity, high viscosity index, low carbon residue, and good oxidation resistance, but its pour point is too high for it to be of value as a lubricant without further treatment.

The high pour point of all these condensation products is probably due partly to the presence of unchlorinated paraffin wax in the chloroparaffin

mixture and partly to the formation of solid long-chain paraffins during the reaction by the condensation of two chloroparaffin molecules. Attempts made to separate these high-melting-point components by conventional solvent dewaxing methods were only partly successful, better results being obtained by vacuum distillation.

TABLE I.

| | Toluene-monochloro-paraffin product, Expt. A/W 37. | Commercial light motor oil. | Commercial hydro-genated motor oil. |
|---|---|---|---|
| Specific gravity, 60° F. | 0·883 | 0·888 | 0·888 |
| Refractive index, $N_D^{20}$ | 1·4960 | — | 1·4910 |
| Viscosity at 100° F. (centistokes, cs.) | 76 | 97·6 | 156 |
| ,, 200° F. ( ,, ) | 11·7 | 13·0 | 16 |
| Viscosity index | 120 | 110 | 90 |
| Viscosity–gravity constant | 0·819 | 0·822 | 0·814 |
| Pour point, ° F. | 80 | 20 | — |
| Conradson carbon, per cent. | 0·09 | 0·37 | 0·23 |
| *Oxidation.* | | | |
| Conradson carbon after oxidation, per cent. | 0·36 | — | 0·48 |
| Viscosity at 100° F. after oxidation (Air-Ministry test), cs. | 104 | — | 161 |
| Oxidation–viscosity ratio | 1·37 | — | 1·03 |
| Sludge after oxidation, per cent. | nil | — | nil |

Vacuum distillation effected the removal of a good deal of solid material, the residual fractions above 300° C./3 mm. being viscous oils, with a red, green, or blue fluorescence. The percentage yields calculated on the basis of the ratio of oil obtained to the maximum theoretical yield are given in Table II.

TABLE II.

| | Expt. A/W 40. | Expt. A/W 37. | Expt. A/W 38. | Expt. A/W 36. |
|---|---|---|---|---|
| Aromatic component | Benzene | Toluene | Naph-thalene | Toluene ($AlCl_3$ catalyst) |
| Total yield, gm. | 346 | 353 | 216 | 170 |
| Waxy oil fraction below 300° C./3 mm., gm. | 230 | 237 | 120 | 111 |
| Viscous oil, residual fraction above 300° C./3 mm., gm. | 116 | 116 | 96 | 59 |
| Percentage yield of total oil | 69·2 | 70·6 | 43·2 | 34·0 |
| Percentage yield of waxy distillate | 46·0 | 47·4 | 24·0 | 22·2 |
| Percentage yield of residual oil | 23·2 | 23·2 | 19·2 | 11·8 |

From the data in Table II it will be seen that, with metallic aluminium as catalyst, total yields of 70 per cent. were obtained in the condensation of monochloroparaffin with benzene and toluene. The ratio of viscous residual oil to waxy distillate was approximately 1 : 2, giving a final yield of high-molecular-weight residual oil of 23 per cent. With naphthalene the total

yield was reduced to 43 per cent., but the ratio of residual oil to waxy distillate was higher, being 1 : 1·25, so that the final yield of residual oil was approximately 19 per cent. This reduced total yield may be accounted for by the higher temperature necessary to initiate the reaction, which may favour the formation of the heavy sludge. The higher residual oil ratio may be due to the formation of oil by thermal dechlorination of the chloroparaffins during the relatively long induction period.

The use of aluminium chloride as catalyst caused much greater sludge formation, although the reaction was carried out at room temperature. This resulted in the total yield of oil being reduced to 34 per cent. The ratio of residual oil to waxy distillate was the same as with the metallic catalyst—approximately 1 : 2.

## Properties of Residual Fractions above 300° C./3 mm.

The properties of three residual oils prepared by the condensation of monochloroparaffin with benzene, toluene, and naphthalene using aluminium metal as catalyst, together with those of the condensation product of monochloroparaffin and toluene with aluminium chloride as catalyst, are given in Table III, and are each compared with commercial lubricating oils of similar viscosity at 100° F.

Table III.

| | Expt. A/W 40. Residual fraction above 300° C./3 mm. | Commercial lubricating oil, A. | Commercial lubricating oil, C. | Expt. A/W 37. Residual fraction above 300° C./3 mm. | Commercial lubricating oil, B. | Expt. A/W 36. Residual fraction above 300° C./3 mm. | Commercial bright stock. | Expt. A/W 38. Residual fraction above 300° C./3 mm. |
|---|---|---|---|---|---|---|---|---|
| Aromatic component | Benzene | — | — | Toluene | — | Toluene ($AlCl_3$) | — | Naphthalene |
| Specific gravity, 60° F. | 0·897 | 0·926 | 0·910 | 0·900 | 0·905 | 0·898 | 0·945 | 0·952 |
| Refractive index, $N_D^{20}$ | 1·5020 | 1·5150 | — | 1·5075 | 1·5005 | 1·5020 | 1·5260 | 1·5230 |
| Viscosity at 100° F., cs. | 399 | 341 | 346 | 449 | 449 | 645 | 729 | 5185 |
| ,, 200° F., cs. | 36·2 | 17·7 | 30·9 | 38·4 | 28·6 | 54·2 | 35 | 223 |
| Viscosity index | 110 | 70 | 105 | 110 | 100 | 115 | 55 | — |
| Viscosity–gravity constant | 0·811 | 0·873 | 0·833 | 0·811 | 0·826 | 0·805 | 0·874 | 0·856 |
| Pour point, ° F. | 55 | 5 | −5 | 55 | — | 55 | 30 | 55 |
| Conradson carbon, per cent. | 0·32 | 0·26 | 0·70 | 0·46 | 0·91 | 0·56 | 2·36 | 7·58 |
| *Oxidation.* | | | | | | | | |
| Conradson carbon after oxidation, per cent. | 1·49 | — | — | 1·27 | — | 1·36 | 4·07 | 8·13 |
| Viscosity at 100° F. after oxidation, cs. | — | — | — | 590 | — | 850 | 952 | 6350 |
| Oxidation–viscosity ratio | — | — | — | 1·31 | — | 1·32 | 1·31 | 1·23 |

The specific gravities, refractive indices, and viscosities of these synthetic oils appear to depend to a large extent on the aromatic hydrocarbon used in their preparation, these properties increasing in the order benzene, toluene, and naphthalene. The viscosity–temperature stabilities are high, the benzene and toluene derivatives having viscosity indices of 110. The viscosity–gravity constants of the benzene and toluene products are similar to the values for paraffinic base oils. The Conradson carbon residues of the

benzene and toluene products are low and compare favourably with commercial lubricating oils. The naphthalene oil has a high carbon residue, but this is not excessive when its high viscosity is considered. The oxidation resistance of the synthetic oils is good, and less change in colour occurs than with the mineral oils used for comparison. Sludge determinations indicated that in all cases no sludge was formed under the oxidation conditions of the test. The low increase in carbon residue after oxidation is good for the benzene and toluene derivatives.

The use of aluminium chloride as catalyst results in the formation of an oil different from, and somewhat inferior to, that obtained with the metallic catalyst. The viscosity of the aluminium chloride product is higher than that of the corresponding oil obtained with the aluminium catalyst, the viscosity index is approximately the same, and the carbon residues, before and after oxidation, are inferior. The yield is only one half of that obtained with the aluminium catalyst.

### Condensation of Aromatic Hydrocarbons with Chlorinated Paraffin Wax of 17 per cent. Chlorine Content.

*Experiment A/W 42.*

Chlorinated paraffin wax containing approximately 17 per cent. chlorine, and corresponding analytically to dichloroparaffin, was condensed with benzene using aluminium metal as catalyst. The procedure was similar to that described in detail previously, petroleum ether, b.pt. 100–120° C., being used as diluent and a minute quantity of iodine added as a promoting agent. The mixture was refluxed until reaction commenced, the reaction was then completed by gently heating until no further fumes of hydrogen chloride were evolved, and the products were allowed to settle. Sludge was separated by decanting off the upper liquid layer and centrifuging. The product was water-washed, filtered through floridin earth, and the diluent removed by distillation. The product was an oil with a pour point of 80° F. The solid hydrocarbons were removed by vacuum distillation, the residual fraction above 300° C./3 mm. being a viscous oil with green fluorescence. The distillate fractions consisted of a white wax together with a pale mobile oil.

The yields of the products are given in Table IV, and are compared with those from the condensation of monochloroparaffin and benzene.

Table IV.

| | Expt. A/W 42. | Expt. A/W 40. |
|---|---|---|
| Chloroparaffin | Di- | Mono- |
| Aromatic hydrocarbon | Benzene | Benzene |
| Total yield, gm. | 319 | 346 |
| Yield of distillate fraction up to 300° C./3 mm., gm. | 142 | 230 |
| Yield of residual oil above 300° C./3 mm., gm. | 177 | 116 |
| Percentage yield of unfractionated oil | 69 | 69·2 |
| Percentage yield of waxy distillate | 30·6 | 46·0 |
| Percentage yield of residual oil | 38·1 | 23·2 |

*Experiment A/W 41.*

A similar condensation was carried out with dichloroparaffin and naphthalene. The reaction was initiated by heating without diluent, petroleum ether diluent being added after the reaction had commenced. The product was a dark brown oil with a pour point of 85° F. Vacuum distillation resulted in the removal of a good deal of wax, together with a green distillate oil, and left an extremely viscous dark oil as the residual fraction.

The total yield by weight was less than that obtained with the monochloroparaffin, owing to the higher chlorine content, but the yield of unfractionated oil calculated as a percentage of the theoretical conversion was approximately the same for both mono- and di-chloroparaffin, being 70 per cent. in each case. The ratio of residual oil to waxy distillate was higher—1 : 0·8—so that the percentage yield of high-molecular-weight residual oil was appreciably higher, being 38 per cent., as compared with 23 per cent. for the monochloroparaffin oil.

The properties of the dichloroparaffin condensation products are given in Table V. The naphthalene oil was unsatisfactory and did not justify a complete analysis.

TABLE V.

| | Expt. A/W 42. | Expt. A/W 41. |
|---|---|---|
| Aromatic component | Benzene | Naphthalene |
| Specific gravity, 60° F. | 0·903 | 0·981 |
| Refractive index, $N_D^{20}$ | 1·5050 | — |
| Viscosity at 100° F., cs. | 813 | 5500 |
| ,, 200° F., cs. | 60 | — |
| Viscosity index | 110 | — |
| Viscosity–gravity constant | 0·809 | 0·907 |
| Pour point, ° F. | 55 | 50 |
| Conradson carbon, per cent. | 0·51 | 14·0 |
| Conradson carbon after oxidation, per cent. | 1·31 | — |

The properties of the dichloroparaffin–benzene oil are similar to those of the monochloroparaffin–benzene product, but the dichloroparaffin–naphthalene oil compared unfavourably with the corresponding monochloroparaffin derivative.

## CONDENSATION OF AROMATIC HYDROCARBONS WITH CHLORINATED PARAFFIN WAX CONTAINING 25 PER CENT. CHLORINE.

*Experiment A/W 29.*

Chlorinated paraffin wax containing 25 per cent. chlorine, and corresponding analytically to trichloroparaffin, was condensed with benzene, using metallic aluminium as catalyst. The procedure was similar to that described for previous condensations with benzene. The product was a viscous oil, liquid at room temperature, and was therefore not subjected to vacuum distillation for removal of solid hydrocarbons. The oil had a clear amber colour.

*Experiment A/W* 33.

A similar experiment was performed, using toluene for the aromatic component, the product resembling that obtained with benzene. The oil was transparent and yellow in colour.

*Experiment A/W* 186.

Naphthalene was also condensed with the trichloroparaffin. Owing to the higher temperature required for the reaction to proceed, it was necessary to use a high-boiling diluent; for this purpose a high-grade kerosine, which had been treated with several batches of concentrated sulphuric acid, water-washed, and redistilled, was employed. The final product was a viscous oil with a blue fluorescence.

The properties of these three synthetic oils are given in Table VI and for comparison those of three commercial lubricants of similar viscosity at 100° F. are also listed.

TABLE VI.

| | Expt. A/W 29. | Commercial motor oil, A. | Expt. A/W 33. | Commercial lubricating oil, B. | Expt. A/W 18b. | Commercial bright stock. |
|---|---|---|---|---|---|---|
| Aromatic hydrocarbon | Benzene | | Toluene | | Naphthalene | |
| Specific gravity, 60° F. | 0·907 | 0·926 | 0·914 | 0·905 | 0·917 | 0·945 |
| Refractive index, $N_D^{20}$ | 1·5065 | 1·5150 | 1·5100 | 1·5005 | 1·5180 | 1·5260 |
| Viscosity at 100° F., cs. | 302 | 341 | 440 | 449 | 815 | 729 |
| Viscosity at 200° F., cs. | 29·1 | 17·7 | 36·6 | 28·6 | 56·6 | 35 |
| Viscosity index | 110 | 70 | 105 | 100 | 105 | 55 |
| Viscosity–gravity constant | 0·831 | 0·873 | 0·834 | 0·826 | 0·830 | 0·874 |
| Pour point, ° F. | 55 | 5 | 55 | — | 50 | 30 |
| Conradson carbon, per cent. | 0·28 | 0·98 | 0·15 | 0·91 | 1·90 | 3·36 |
| *Oxidation.* | | | | | | |
| Conradson carbon after oxidation, per cent. | 0·69 | — | 0·48 | — | 2·08 | 4·07 |
| Viscosity at 100° F. after oxidation, cs. | 416 | — | 616 | — | 1·020 | 952 |
| Oxidation–viscosity ratio | 1·38 | — | 1·40 | — | 1·25 | 1·31 |
| Total yield, gm. | 270 | — | 280 | — | 220 | — |
| Yield, percentage of theoretical | 63·5 | — | 66 | — | 51·8 | — |

The specific gravities of the synthetic oils are of the same order as those of commercial lubricants of comparable viscosity at 100° F., and increased with increasing molecular weight of the aromatic component. The viscosities increased in the order benzene, toluene, and naphthalene. The viscosity–temperature stabilities are uniformly high, the synthetic oils having vis-

cosity indices of 105–110. The viscosity–gravity constants ranked the oils as essentially paraffinic base. The pour points are high, 50–55° F., but can be improved by vacuum distillation, the residual fractions above 300° C./3 mm. having a pour point of 25–30° F. The Conradson carbon residues of the benzene and toluene derivatives are low, the synthetic oils being superior in this respect to petroleum lubricants of similar viscosity at 100° F. Excellent oxidation resistance is shown by the synthetic oils, which exhibit comparatively little change in colour and give no sludge formation. The increase in Conradson carbon after oxidation is, in all cases, good. The increase in viscosity after oxidation is moderate, the ratios of the viscosity of the oxidized oil to that of the original oil varying from 1·25 to 1·4.

### Influence of Chlorine Content of Chlorinated Paraffin Wax on Condensation Oils.

In Table VII the properties of the oils obtained by condensing monochloroparaffin and trichloroparaffin with toluene are compared to show the effect of varying chlorine content in the chlorinated paraffin wax.

Table VII.

| | Expt. A/W 35. Unfractionated condensation product. | Expt. A/W 33. Unfractionated condensation product. |
|---|---|---|
| Chlorine content of chlorinated paraffin wax, per cent. | 10 | 25 |
| Chloroparaffin | Mono- | Tri- |
| Aromatic component | Toluene | Toluene |
| Yield, percentage of theoretical conversion | 70·6 | 66 |
| Specific gravity, 60° F. | 0·883 | 0·914 |
| Refractive index, $N_D^{20}$ | 1·4960 | 1·5100 |
| Viscosity at 100° F., cs. | 76 | 440 |
| ,, 200° F., cs. | 11·7 | 36·6 |
| Viscosity index | 120 | 105 |
| Viscosity–gravity constant | 0·819 | 0·834 |
| Pour point, ° F. | 80 | 55 |
| Conradson carbon, per cent. | 0·09 | 0·15 |
| *Oxidation.* | | |
| Conradson carbon after oxidation, per cent. | 0·36 | 0·48 |
| Viscosity at 100° F. after oxidation, cs. | 104 | 616 |
| Oxidation–viscosity ratio | 1·37 | 1·40 |
| Sludge formation, per cent. | nil | nil |

The properties of residual oils above 300° C./3 mm., prepared by condensing chlorinated paraffin waxes of varying chlorine content with benzene and toluene and then subjecting the refined products to vacuum distillation, are listed in Table VIII. For comparison purposes the trichloroparaffin–toluene oil was distilled up to 300° C./3 mm. and the properties of the residual fraction determined.

It will be seen from these two tables that the specific gravity, refractive index, and viscosity of the condensation oils increased with the chlorine content of the chloroparaffin used. The viscosity index appears to decrease with increasing chlorine content of the chloroparaffin used. The

pour point decreased with increasing chlorine content of the chloroparaffin component. This would be expected from the reduction in unchlorinated wax present in the higher chloroparaffins and the diminished possibility of long straight-chain paraffins being formed by the condensation of two chloroparaffin molecules. The viscosity–gravity constant increased with the chlorine content of the raw material corresponding with increased cyclisation and branching. The Conradson carbon and oxidation stability is but little affected by the chlorinated wax used.

TABLE VIII.

| | Expt. A/W 40. Residual fraction above 300° C./ 3 mm. | Expt. A/W 42. Residual fraction above 300° C./ 3 mm. | Expt. A/W 37. Residual fraction above 300° C./ 3 mm. | Expt. A/W 35. Residual fraction above 300° C./ 3 mm. | Expt. A/W 33. Residual fraction above 300° C./ 3 mm. |
|---|---|---|---|---|---|
| Chlorine content of chloroparaffin component, per cent. | 10 | 17·5 | 10 | 12·5 | 25 |
| Chloroparaffin | Mono- | Di- | Mono- | — | Tri- |
| Aromatic hydrocarbon | Benzene | Benzene | Toluene | Toluene | Toluene |
| Yield, percentage of theoretical conversion | 23·2 | 37·2 | 23·2 | 27·7 | 50 |
| Specific gravity, 60° F. | 0·897 | 0·903 | 0·900 | 0·908 | 0·933 |
| Refractive index, $N_D^{20}$ | 1·5020 | 1·5050 | 1·5075 | 1·5080 | 1·5210 |
| Viscosity at 100° F., cs. | 399 | 813 | 449 | 644 | 3270 |
| ,, 200° F., cs. | 36·2 | 60 | 38·4 | 47·3 | 144 |
| Viscosity index | 110 | 110 | 110 | 105 | — |
| Viscosity–gravity constant | 0·811 | 0·809 | 0·814 | 0·820 | 0·859 |
| Pour point, ° F. | 55 | 50 | 55 | 55 | 30 |
| Conradson carbon, per cent. | 0·32 | 0·51 | 0·46 | 0·45 | 0·43 |
| *Oxidation.* | | | | | |
| Conradson carbon after oxidation, per cent. | 1·49 | 1·31 | 1·27 | 1·14 | — |
| Viscosity at 100° F. after oxidation, cs. | — | — | 590 | 732 | — |
| Oxidation–viscosity ratio | — | — | 1·31 | 1·14 | — |

The increase in specific gravity, refractive index, viscosity, and viscosity–gravity constant with increase in chlorine content of the chlorinated wax agrees with accumulation of simple cyclic groups in the molecule, and supports the hypothesis that the principal reaction during the condensation is replacement of chlorine by aromatic rings.

## INFLUENCE OF THE AROMATIC HYDROCARBON COMPONENT ON THE CONDENSATION OILS.

Mention has already been made of the difference in the lengths of the preliminary induction periods with benzene, toluene, and naphthalene. In the case of benzene the reflux temperature was reduced by its relatively lower boiling point, so that a slightly increased induction period would be expected, but naphthalene, even at a much higher reflux temperature than toluene or benzene, reacted less readily. The effect of the aromatic component on the properties of the condensation oils is shown in Table IX.

TABLE IX.

| | Expt. A/W 40. Residual fraction above 300° C./3 mm. | Expt. A/W 37. Residual fraction above 300° C./3 mm. | Expt. A/W 38. Residual fraction above 300° C./3 mm. | Expt. A/W 42. Residual fraction above 300° C./3 mm. | Expt. A/W 41. Residual fraction above 300° C./3 mm. | Expt. A/W 29a. Unfractionated condensation product. | Expt. A/W 33. Unfractionated condensation product. | Expt. A/W 18b. Unfractionated condensation product. |
|---|---|---|---|---|---|---|---|---|
| Aromatic hydrocarbon . | Benzene | Toluene | Naphthalene | Benzene | Naphthalene | Benzene | Toluene | Naphthalene |
| Chloroparaffin . . | Mono- | Mono- | Mono- | Di- | Di- | Tri- | Tri- | Tri- |
| Yield, percentage of theoretical conversion | 23·2 | 23·2 | 19·2 | 37·2 | 20·0 | 63·5 | 66 | 51·8 |
| Specific gravity, 60° F | 0·897 | 0·900 | 0·952 | 0·903 | 0·961 | 0·907 | 0·914 | 0·917 |
| Refractive index, $N_D^{20°}$ . | 1·5020 | 1·5075 | 1·5220 | 1·5050 | — | 1·5065 | 1·5100 | 1·5180 |
| Viscosity at 100° F., cs. | 399 | 449 | 5185 | 813 | 5500 | 302 | 440 | 815 |
| ,, 200° F., cs. | 36·2 | 38·4 | 223 | 60·0 | — | 29·1 | 36·6 | 56·6 |
| Viscosity index . . | 110 | 110 | — | 110 | — | 110 | 105 | 105 |
| Viscosity–gravity constant . . . | 0·811 | 0·814 | 0·856 | 0·809 | 0·907 | 0·831 | 0·834 | 0·830 |
| Pour point, ° F. . . | 55 | 55 | — | 55 | — | 55 | 55 | 50 |
| Conradson carbon, per cent. . . . | 0·32 | 0·46 | 7·58 | 0·51 | 14·05 | 0·28 | 0·15 | 1·90 |
| *Oxidation.* | | | | | | | | |
| Conradson carbon after oxidation, per cent. . | 1·49 | 1·27 | 8·13 | 1·31 | — | 0·69 | 0·43 | 2·08 |
| Viscosity at 100° F. after oxidation, cs. . | — | 590 | 6350 | — | — | 416 | 616 | 1020 |
| Oxidation–viscosity ratio . . . | — | 1·31 | 1·23 | — | — | 1·38 | 1·40 | 1·25 |

The percentage yield is approximately the same for the benzene and the toluene derivatives, but the yield is greatly reduced when naphthalene is used for the aromatic component. The specific gravity increased in the order benzene, toluene, and naphthalene, and for the residual oils above 300° C./3 mm. the gravity of the naphthalene derivative is considerably higher than those of the products from the simple aromatics. The refractive index increased similarly in the normal order of the aromatic components—benzene, toluene, and naphthalene. The viscosities also followed the same order of increase, the viscosities of the residual naphthalene oils being considerably greater than those of the corresponding benzene and toluene oils. The viscosity–temperature coefficients, as evaluated by the viscosity indices, are fairly uniform, 105–110, but the viscosities of the residual naphthalene oils were completely beyond the range of viscosity index calculations. The viscosity–gravity constants of the residual benzene and toluene oils ranked them as "paraffinic," but the naphthalene residual oils have constants similar to those of "naphthenic" oils. The pour points of the synthetic oils are all of the order 50–55° F. The carbon-forming tendencies of all the benzene and toluene oils are low. The naphthalene oils have much higher carbon residues. The increase in carbon residue after oxidation is of approximately the same order for the benzene, toluene, and naphthalene oils, and is somewhat higher for the residual oils than for the undistilled oils. The increase in viscosity after oxidation is approximately the same for the benzene, toluene, and naphthalene derivatives, the oxidation–viscosity ratios being 1·23–1·40.

### INFLUENCE OF THE CATALYST ON THE CONDENSATION PRODUCTS.

Condensations were carried out with anhydrous aluminium chloride as catalyst, so that comparison could be made with the metallic aluminium

catalyst used in the previous experiments. It was found also that the sludge formed in condensation reactions with the metallic catalyst could be used as a condensation catalyst. Small amounts of iodine, though not essential for reaction to occur, tend to shorten the preliminary induction period. The products obtained with aluminium and aluminium chloride catalysts are compared in Table X.

TABLE X.

| | Expt. A/W 37. Residual fraction above 300° C./ 3 mm. | Expt. A/W 36. Residual fraction above 300° C./ 3 mm. | Expt. A/W 18. Unfractionated condensation product. | Expt. A/W 15. Unfractionated condensation product. | Expt. A/W 16. Unfractionated condensation product. |
|---|---|---|---|---|---|
| Catalyst | Aluminium | Aluminium chloride | Aluminium | Aluminium chloride | Aluminium chloride |
| Aromatic component | Toluene | Toluene | Naphthalene | Naphthalene | Naphthalene |
| Chloroparaffin | Mono- | Mono- | Tri- | Tri- | Tri- |
| Reaction temperature (maximum), ° C. | 115 | 20 | 150 | 45 | 20 |
| Yield, percentage of theoretical conversion. | 23·2 | 11·8 | 51·8 | — | — |
| Specific gravity, 60° F. | 0·900 | 0·898 | 0·917 | Product | Product |
| Refractive index, $N_D^{20}$ | 1·5075 | 1·5020 | 1·5180 | is an | is an |
| Viscosity at 100° F., cs. | 449 | 645 | 815 | asphaltic | asphaltic |
| ,, 200° F., cs. | 38·4 | 54·2 | 56·6 | solid | solid |
| Viscosity index | 110 | 115 | 105 | | |
| Viscosity–gravity constant | 0·814 | 0·805 | 0·830 | | |
| Pour point, ° F. | 55 | 55 | 50 | | |
| Conradson carbon, per cent. | 0·46 | 0·56 | 1·90 | | |
| *Oxidation.* | | | | | |
| Conradson carbon after oxidation, per cent. | 1·27 | 1·36 | 2·08 | | |
| Viscosity at 100° F. after oxidation, cs. | 590 | 850 | 1020 | | |
| Oxidation–viscosity ratio | 1·31 | 1·32 | 1·25 | | |

In the case of the monochloroparaffin–toluene oils, using aluminium metal or aluminium chloride as catalyst, the products have very similar properties, but the yield is much higher with the metallic catalyst. With naphthalene and trichloroparaffin very different results are obtained from the two catalysts. The condensation using metallic aluminium yields a viscous oil with good properties, but with aluminium chloride the product is a solid asphaltic or rubber-like material.

Aluminium chloride is extremely reactive, and, in addition to the condensation of alkyl chloride with aromatic hydrocarbon, it may induce dehydrogenation and polymerization reactions. Side reactions of this nature appear to have taken place in the experiments using aluminium chloride. In the case of the monochloroparaffin–toluene condensation, the amount of heavy sludge is increased and the yield of oil obtained is considerably reduced. With naphthalene and trichloroparaffin the side

reactions appear to have predominated to the exclusion of the simple condensation.

The properties of the products obtained, using the sludge from a previous experiment, alone and together with fresh metallic aluminium, are compared with the normal condensation oils in Table XI.

TABLE XI.

| | Expt. A/W 25. Unfractionated condensation product. | Expt. A/W 26. Unfractionated condensation product. | Expt. A/W 27. Unfractionated condensation product. |
|---|---|---|---|
| Catalyst | Al | Al plus sludge from A/W 25 | Sludge from A/W 26 |
| Aromatic component | Benzene | Benzene | Benzene |
| Chloroparaffin | Tri- | Tri- | Tri- |
| Yield, per cent. of theoretical | 42·5 | 68 | 25 |
| Reaction temperature (maximum), ° C. | 110 | 50 | 50 |
| Specific gravity, 60° F. | 0·898 | 0·880 | 0·884 |
| Refractive index, $N_D^{20}$ | 1·5025 | 1·4930 | 1·4935 |
| Viscosity at 100° F., cs. | 241 | 136 | 113 |
| ,, 200° F., cs. | 25·8 | 18·6 | 16·1 |
| Viscosity index | 115 | 125 | 125 |
| Viscosity–gravity constant | 0·822 | 0·806 | 0·813 |

Sludge from a previous condensation can be used as a catalyst, although its use in this respect, as will be seen from the table, results in the formation of an oil of lower viscosity but improved viscosity index and V.G.C.

Extreme subdivision of the metallic catalyst and the removal of the oxide film protecting the metal were found to have an adverse effect on the products. An experiment was performed using trichloroparaffin and naphthalene with finely divided aluminium powder. Reaction commenced at 150° C., and the mixture was then allowed to cool slowly, but an extremely vigorous reaction commenced, and the final product was a greyish, rubber-like material closely resembling that obtained using aluminium chloride as a catalyst with naphthalene and trichloroparaffin.

In another experiment the aluminium metal was treated with sodium hydroxide solution, then washed with distilled water, absolute alcohol, and petroleum ether. Benzene and trichloroparaffin were used in this condensation, and the final product was a dark-brown viscous oil. This oil did not respond to bleaching-earth treatment, and appeared to contain undesirable resinic and asphaltic material. Preliminary removal of the alumina film or etching of the catalyst with caustic soda therefore appears to result in the formation of inferior products.

The relative efficiencies of aluminium, activated aluminium, and aluminium chloride were investigated for a simple reaction of the Friedel–Crafts type, in which *iso*propyl benzene was prepared by the condensation of *iso*propyl bromide and benzene.

The amount of catalyst used was one-tenth molar calculated on the weight of *iso*propyl bromide. With the metallic catalysts, 60 gm. *iso*propyl

bromide were refluxed with excess benzene (145 c.c.) until reaction commenced. The preparation was completed by refluxing for 5–7 hr., settling, hydrolysing the upper liquid layer, and fractionally distilling the product. With aluminium chloride the reaction proceeded without preliminary heating, 60 gm. of the *iso*propyl bromide being added slowly to a mixture of the catalyst and excess benzene (145 c.c.).

The activated aluminium (*i.e.*, aluminium–mercury couple) was prepared by etching aluminium filings with dilute caustic-soda solution, washing with water, and then treating with a 0·5 per cent. mercuric chloride solution for 2 min. The catalyst was then washed with water, alcohol, and ether, and stored under benzene.

The fraction from the condensation reaction boiling at 147–157° C. was considered to consist essentially of *iso*propyl benzene, the refractive indices confirming this. The yields calculated on this assumption are given in the table below, together with the amount of unreacted benzene.

TABLE XII.

| Catalyst. | Yield of *iso*propyl benzene, c.c. | Unreacted benzene recovered, c.c. |
|---|---|---|
| $AlCl_3$ . . . . . | 32 | 65 |
| Al . . . . . | 40 | 70 |
| Al–Hg couple . . . | 37 | 73 |

The highest yield was given by the metallic aluminium catalyst. The amount of *iso*propyl benzene and also of unreacted benzene was least in the case of the aluminium chloride catalyst, so that the use of this more reactive material resulted in the formation of a greater proportion of high-boiling compounds and sludge.

These experiments confirmed to a certain extent the results obtained with the chloroparaffin condensations using aluminium and aluminium chloride catalysts, and indicated that the activation of the aluminium did not improve the yields. The use of the more complex chlorinated waxes naturally resulted in a greater disparity between the metallic and halide catalysts, simple organic halides such as *iso*propyl bromide offering less scope for the dehydrogenation and polymerization side reactions, which occur with the aluminium chloride catalyst.

## By-Products of the Condensation Reaction.

It has been mentioned previously that the reaction products, on cooling and settling, separate into two layers. The upper layer is utilized for the preparation of the synthetic oils, whilst the lower layer consists of a viscous black sludge. This sludge is only slowly decomposed by water, and for complete hydrolysis hot water and agitation are required. The hydrolysis product is a dark viscous asphaltic material.

## Composition of the Sludge.

The sludge is saturated with hydrochloric acid formed during the reaction, and fumes on exposure to air. Analysis of a typical sludge from

Experiment A/W 33 was carried out by dissolving a weighed amount of sludge in benzene, passing a stream of nitrogen through the solution for several hours in order to remove the hydrochloric acid, and then refluxing gently for 2 hr. with a 2 per cent. solution of sulphuric acid. The aqueous extract was separated and filtered. Chloride was determined volumetrically by the Volhard method and aluminium was estimated gravimetrically, using 8-hydroxyquinoline. The analytical results obtained were:—

| | |
|---|---|
| Chlorine . . . | 13·83 per cent. |
| Aluminium . . . | 2·72 per cent. |

These percentages correspond to a chlorine–aluminium atomic ratio of 3·86 : 1. It is probable that the hydrogen chloride was not removed quantitatively by the nitrogen blowing and that the sludge is an organic aluminium-chloride double compound of the type $AlCl_3 \cdot R$. This compound contains a high proportion of organic radical, *R*, corresponding to 83·45 per cent. The total molecular weight of the organic radical is at least 860, and corresponds, therefore, to approximately 60 carbon atoms.

### Formation of Green Colouring Compound.

It was observed that the heavy sludge from several of the condensation experiments, after standing for several months in corked bottles, developed in parts an intensely bright green coloration, in marked contrast to its general black appearance. This green material was extracted by washing with petroleum ether; then, after removal of the solvent, the residual oil was observed to possess a bright malachite-green fluorescence in daylight. Addition of small amounts—0·1–0·5 per cent.—of this colouring material to pale distillate oils and water-white heavy paraffin imparted to them a bright green fluorescent bloom.

Similar fluorescent materials are formed by the action of aluminium chloride on naphthalene, anthracene, and other polycyclic hydrocarbons. It is possible that in the condensation reaction the aluminium chloride–organic complex reacts to give coloured compounds, probably of condensed polycyclic structure.

### Summary and Conclusions.

#### *General.*

Chlorinated paraffin waxes can be condensed with aromatic hydrocarbons, using metallic aluminium as catalyst to give viscous hydrocarbon oils. The oils have high viscosity indices, and the viscosity–gravity constants are in many cases comparable to those of paraffin base oils. The Conradson carbon residues of the benzene and toluene condensation oils are extremely low. All the condensation oils have good oxidation resistance; after oxidation the change in colour is small, no asphalt is deposited, and the increase in viscosity is similar to that of commercial motor lubricants.

#### *Influence of Chlorine Content of the Chlorinated Paraffin Wax.*

The chlorinated waxes corresponding analytically to mono- and di-chloroparaffin give condensation products which are solid at room

temperature. The physical properties of an unfractionated condensation oil are in accordance with its paraffin-wax content—the specific gravity, refractive index, viscosity, and viscosity index being lower than the corresponding values for the synthetic oils derived from trichloroparaffin. The yield of high-molecular-weight material, boiling above 300° C./3 mm., increases with increasing chlorine content of the chlorinated paraffin wax. The specific gravity, refractive index, viscosity, and viscosity–gravity constant also increase with increase in the chlorine content of the chloroparaffin component. The viscosity index and the pour point decrease for the higher chloroparaffin derivatives.

*Influence of the Aromatic Hydrocarbon Component.*

Naphthalene reacts less readily than benzene or toluene, and requires a longer preliminary induction period. The yields are approximately the same for the benzene and toluene derivatives, but the yield of the naphthalene oil is considerably less. The specific gravity, refractive index, viscosity, and viscosity–gravity constant increase in the order of the molecular weights of the aromatic components. The viscosity indices are fairly uniform—105–110—but the viscosities of the residual naphthalene oils above 300° C./3 mm. are beyond the range of viscosity-index calculations. The carbon residues of all the benzene and toluene oils are low, but the naphthalene oils have high carbon residues.

*Influence of the Catalyst.*

The metallic aluminium catalyst gives higher yields than aluminium chloride. The latter catalyst causes the formation of excessive quantities of sludge, and in the case of naphthalene condensed with trichloroparaffin the product is a rubber-like or asphaltic material. The heavy sludge can be used as catalyst, and produces oils similar to those obtained with aluminium as catalyst, but, unless used in conjunction with the metal, the yield decreases.

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# THE MANUFACTURE AND USE OF TETRA-ETHYL-LEAD.*

By Graham Edgar.†

Gasoline containing tetraethyl-lead was first put on public sale at a single service station in Dayton, Ohio, on 1st February, 1923, under the now familiar name of "ethyl" gasoline.

Fig. 1 shows the sales in the United States of ethyl gasoline, leaded regular gasoline, leaded and total aviation gasoline, and total figures of

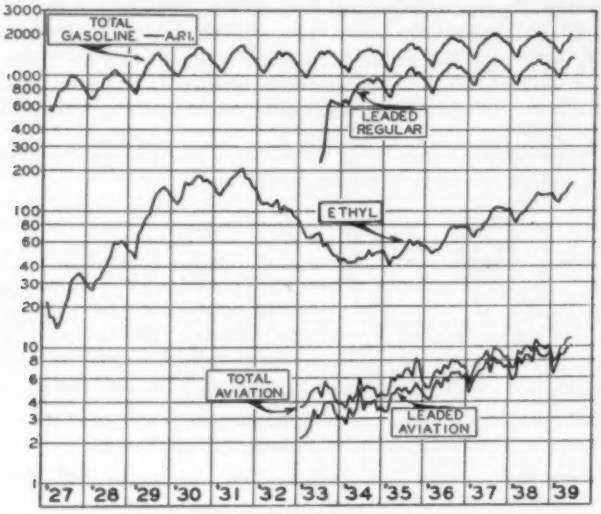


Fig. 1.

Gasoline consumed in the United States (millions of gallons).

the American Petroleum Institute for gasoline sales from 1927 through the first half of 1939. They show that the sales of ethyl gasoline reached a maximum in 1931; that the decline which followed was not affected measurably by the introduction of leaded regular gasoline in 1933, and that from 1934 on there has been a steady increase, until at present the gallonage is nearly equal to that of 1931. They show that to-day about 75 per cent. of all gasoline sold in the United States contains tetraethyl-lead. In the aviation field almost all gasoline of 80 octane number or

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* Paper presented to the annual meeting of members of the Institute of Petroleum in U.S.A. at Chicago on 15th November, 1939. (Abridged from *Industrial and Engineering Chemistry*, 1939, **31**, 1439–1446.)

† Ethyl Gasoline Corporation, New York, N.Y.

better contains tetraethyl-lead; in fact, the performance of the modern military and transport plane is due in large part to the development of high-octane gasoline, a development in which tetraethyl-lead played an important rôle.

Outside the United States tetraethyl-lead is used in motor gasoline extensively in Canada (where the percentage of leaded gasoline is equal to that for the United States), England, France, Australia, New Zealand, and Germany, and to a smaller extent in many other countries. In the aviation field it is used in nearly every country in the world for both military and transport purposes. Manufacturing plants are in operation in Germany and France and are planned for other countries, although a share of the foreign demand is still supplied from the United States.

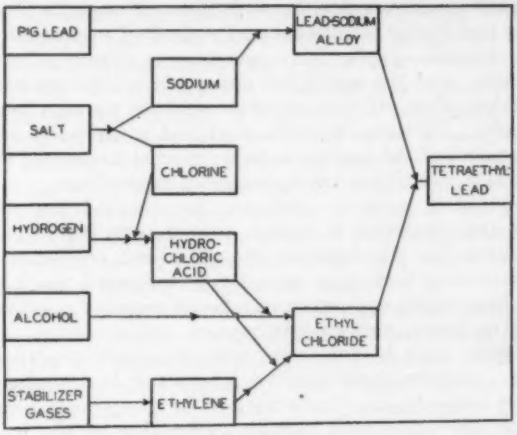


FIG. 2.

FLOW-SHEET OF TETRAETHYL-LEAD MANUFACTURE.

Tetraethyl-lead is manufactured by the reaction of ethyl chloride with an alloy of sodium and metallic lead, and the immediate raw materials are therefore ethyl chloride, sodium, and lead. With the exception of metallic lead, none of these are available commercially in the quantities required, and for this reason, as well as in the interest of manufacturing economy, it was necessary to include their manufacture at Baton Rouge.

Fig. 2 gives a flow-sheet of the manufacturing operations. Salt, obtained from the adjoining works of the Solvay Company, is electrolysed to produce sodium and chlorine. The sodium is melted with lead to form the alloy, which, after grinding, is ready for the final reaction. The chlorine formed in the electrolysis is burned with hydrogen, obtained from the adjoining refinery of the Standard Oil Company of Louisiana, to form gaseous hydrochloric acid.

Ethyl chloride is produced from hydrochloric acid by two distinct processes. The first is the familiar reaction with ethyl alcohol. The second is by reaction with ethylene. In this process, refinery stabilizer

gases consisting largely of propane are cracked and the cracked gases fractionated at low temperatures to separate the ethylene formed. This is allowed to react with hydrochloric acid gas at low temperature in the presence of a catalyst to produce ethyl chloride. The Baton Rouge plant is the first commercial development of this method of manufacturing ethyl chloride. Ethyl chloride produced by either process is subjected to appropriate purification processes and is then ready for the final reaction with the lead–sodium alloy.

The reaction may be represented by the equation:

$$4PbNa + 4C_2H_5Cl = Pb(C_2H_5)_4 + 4NaCl + 3Pb$$

In the manufacturing process the alloy and ethyl chloride are allowed to react at moderate pressures and temperatures. At the completion of the reaction the product is distilled with steam to separate the tetraethyl-lead, and the lead sludge is collected and re-smelted to pig lead. Although the reaction appears simple, this appearance is illusory. Side reactions invariably occur, and the conditions under which the formation of tetraethyl-lead takes place with a minimum of side reaction have required extended study. Furthermore, tetraethyl-lead is thermally unstable, and the closest control of the reaction rate is essential to prevent the initiation of decomposition which may reach dangerous proportions.

Tetraethyl-lead is poisonous and may be absorbed into the body by skin contact and inhalation of vapour, as well as by ingestion. This fact has necessitated the development of specialized equipment and well-controlled operating technique in order to safeguard the health of the operators. Ventilating equipment of unusual capacity must be provided; valves, stuffing-boxes, and gaskets require special design, as an entire absence of leaks must be achieved; and emergency conditions must be provided for. Despite the difficulties inherent in the problem the safety record of the tetraethyl-lead industry has for many years been far better than that of any other lead industry, according to the best available figures.

In addition to tetraethyl-lead, the finished anti-knock fluid requires the addition of ethylene dibromide, ethylene dichloride, and dye. The latter two are purchased in the open market, but an adequate supply of ethylene dibromide at reasonable cost has represented a serious manufacturing problem for many years. Supplies of bromine are limited, and for this reason recourse was had a few years ago to that great reservoir of raw materials, the sea. The dramatic success, both technical and economic, of the Ethyl-Dow plant at Kure Beach, N.C., for producing ethylene dibromide from sea-water, has been described.[1]

Sea-water contains an average of only 67 parts of bromine per million of water, or about 1 lb. of bromine in 7·5 tons of water, but research has been equal to the task of extracting this minute amount. The sea-water is acidified and chlorinated; the bromine is blown out with air and concentrated by absorption, re-liberated from the concentrated solution, recovered by distillation, and finally allowed to react with ethylene to form the desired product, ethylene dibromide.

When ethyl gasoline was first put on the market, the octane-number scale was unknown, and methods of measuring anti-knock value were

uncertain, to say the least. However, it may be safely stated that the anti-knock value of ethyl gasoline, as first sold, was not so high as that of regular-grade gasoline to-day. The ethyl of to-day is about 10 octane numbers better than it was fifteen years ago. An approximately equivalent increase has occurred in the anti-knock value of regular-grade gasoline.

In the past the automotive engine has taken advantage of increasing fuel quality by increasing the compression ratio, which increases both power per cubic inch of displacement and power per gallon of fuel. It is possible that in the future this trend may be the main one which will continue. This trend cannot be followed indefinitely, but it can be pursued very much farther than it has been. For example, several years ago the General Motors Corporation carried out an elaborate research project to determine the possibilities of increasing compression ratio under conditions in which the anti-knock value of the fuel was no longer the limiting factor. An automobile equipped with an overhead-valve engine was selected for the investigation. The car was operated both on the dynamometer and on the road at a number of compression ratios and a number of gear ratios, and fuels were used which in each case were just capable of avoiding knock. The octane numbers of these fuels are a little uncertain, since neither they nor the octane number requirements were determined by the conventional C.F.R. method, but approximately 69 octane fuel was required for the standard 5·25 compression ratio, about 95 octane number for 8·0 compression ratio, and something better than 100 octane number for 10·3 compression ratio.

But increase in compression ratio is only one of the methods by which the automotive engine may utilize fuels of high anti-knock value. In the development of the aircraft engine, where power per cubic inch of displacement is usually more important than thermal efficiency, it has been well demonstrated that a supercharged engine can utilize fuel of as high an anti-knock value as may be available. Already 100 octane number fuel is in wide use, and fuels above 100 octane number are under investigation. Little has been done in supercharging the automobile engine except for special purposes, but there is a good chance that the future may see this development extensively followed.

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# THE TRINIDAD GEOLOGICAL CONFERENCE.

*18th–27th April* 1939.

THIS Conference was convened under the auspices of the Petroleum Association of Trinidad, and received the full co-operation of the Government, represented by the Hon. R. S. MacKilligin, O.B.E., M.C., Mr. Nelson Betancourt, and Mr. W. F. Foster, all of the Mines Department.

Other bodies and corporations which combined their efforts to make the Conference a signal success were—the Geological Service of the Venezuelan Government, the Trinidad Branch of the Institute of Petroleum, and the organizations of the many oil companies operating in the Island.

The full transactions of the Conferences are being published in the *Boletin de Geologia y Minera del Ministerio de Fomento, Caracas, E.U. de Venezuela*, and Dr. H. D. Hedburg has given a short account of the meetings in the *Bulletin of the American Association of Petroleum Geologists*, **23**, 8, August 1939, accompanied by able abstracts of the papers presented.

The objects of the Conference were as follows :—

> "1. To express to the Venezuelan Government the gratitude of the geologists of Trinidad for the generous invitations to the First and Second Venezuelan Geological Congresses; also to the oil companies operating in Venezuela for their liberal scientific contributions to these congresses.
>
> "2. To introduce the geologists of Venezuela to stratigraphical details of the geology of Trinidad on the assumption that interchange of knowledge will be of practical value to all.
>
> "3. To foster the good accord engendered by the Venezuelan Government in establishing closer co-operation and creating a spirit of mutual understanding between the two oil-producing countries on either side of the Gulf of Paria."

An Organizing Committee was constituted as follows :—

| | |
|---|---|
| Chairman . . . . | Hon. R. S. MacKilligin, O.B.E., M.C. |
| Vice-Chairman and Secretary . | E. C. Scott. |
| Excursions . . . . | H. G. Kugler and A. G. Hutchinson. |
| Publications . . . . | C. C. Wilson. |
| Entertainment and Organization | N. Betancourt and A. E. Gunther. |
| Contact . . . . . | P. E. T. O'Connor and R. G. Ffoulkes-Jones. |

Between forty and fifty geologists attended, including Professor V. C. Illing of the Royal School of Mines; Dr. R. Rutsch, Natural History Museum, Basle; Dr. Buess and Dr. Kehrer of the Royal-Dutch Shell, and Dr. H. D. Hedburg of the Gulf Company.

The Venezuelan Geological, Mines Inspectorate, and Public Works Services were represented by nine members, led by Drs. G. Zuloaga and L. Herrera.

The many oil companies operating in Venezuela and Trinidad were also represented by their Geological Staffs. These included over twenty members of the Institute of Petroleum.

Overseas visitors were met at the docks and seaplane base. Proceedings were then opened by a reception given by His Excellency the Acting Governor, the Hon. John Huggins, C.M.G., M.C., at his residence.

The following morning His Excellency the Acting Governor formally opened the Conference with a short speech of welcome, and a visit was then made to the Imperial College of Tropical Agriculture.

On succeeding days six excursions were made to places of interest in the island, including type fossil localities, diagnostic type sections, etc.

These excursions were made mainly in motor buses, and entailed travelling upwards of one hundred miles a day. For the longer excursions, special trains on the Government railway were arranged by the Director of Public Works.

The itineraries and conduct of these field excursions were in the hands of Dr. H. G. Kugler, Chief Geologist to the Central Mining & Investment Corporation, and it was due to his able organization that they proved to be an outstanding success, supported, as they were, by an exact time-table, efficient guide-book and maps, and an absorbing commentary at each scheduled stop.

The weather was very propitious, and an excellent lunch and refreshment service was maintained throughout, with the aid of many local clubs and similar institutions.

The very beautiful scenery of the island was seen at its best, and perhaps the most memorable trip was that taken by launch along the small islands situated between Trinidad and Venezuela, and was made with the object of visiting the island of Patos.

On the two remaining days a series of papers was presented by members. A list of authors and papers follows. (Abstracts of these by Dr. H. D. Hedburg have been referred to previously. Abstracts will also be given in the *Journal* when the complete transactions of the Conference become available.)

| | |
|---|---|
| 1. Kugler, H. G. | "Our Present Knowledge of the Geologic History of Trinidad." |
| 2. Schmid, K. | "The Classification of Rock Units and the Definition of Formations in Trinidad." |
| 3. Hutchinson, A. G., and Terpstra, G. R. J. | "A Note on the Biche Quarry Limestones." |
| 4. Renz, H. H., and Suter, H. H. | "The Pozon and El Mene de Acosta Type Sections of the Agua Salada Formations (Falcon, Venezuela)." |
| 5. Rutsch, R. | "Evolution of Tropical American Tertiary Faunas and Theory of Continental Drift." |
| 6. Hutchinson, A. G. | "Note on the Jurassic in Trinidad, B.W.I." |
| 7. Wilson, C. C. | "Los Bajos Fault of S. Trinidad." |
| 8. Gunther, A. E., and Terpstra, G. R. J. | "A Note on some Recent Additions to the Upper Cretaceous of Trinidad, B.W.I." |
| 9. Senn, A. | "The Paleogene of Barbados and its Bearing on the Antillean Caribbean Region." |

The Chairman, the Hon. R. S. MacKilligin, declared the meeting closed with a valedictory speech. Dr. Guillermo Zuloaga, in a reply of thanks, invited members to a Third Venezuelan Geological Congress to be held in 1940.

E. C. S.

# OBITUARY.

## F. G. EDMED, O.B.E., B.Sc., F.I.C.

THROUGH the death, on the 22nd January, 1940, of Mr. Edmed, for many years Admiralty Chemist, the Institute has lost one of its "official" Honorary Members, who for many years gave us a great deal of valuable help in connection with Standard Methods of Testing. He was a member of the Chemical Standardization Committee and of the Fuel Oil and S.I.T. Panels.

Leaving the Royal College of Science in 1898, he entered the service of the War Office in the Chemical Inspection Department, Woolwich. After the war he transferred to the Admiralty, and took charge of the Chemical Inspection at the Royal Naval Cordite factory, later (1926) succeeding Mr. Arnold Philip as Admiralty Chemist.

His experience in analytical chemistry in these important Government offices had been very extensive, and time and again proved of great value in the work of revision of Standard Methods. Further, he was always ready to have investigations on modifications or the suggested improvement of tests carried out under his supervision.

He was associated with the closely allied work of the British Standards Institution, representing the Admiralty on the Chemical Divisional Council, besides being an active member of the Chemical Glass Ware Panel.

Mr. Edmed was for many years a keen member on the Council of the Institute of Chemistry, but had not sought re-election in the forthcoming ballot owing to increasing indisposition. He was a Vice-President of the Institute from 1933 to 1936. He retired from the position of Admiralty Chemist as recently as 1st January, 1940.

The writer enjoyed the close friendship of Edmed from the time when he left the Royal College of Science. His outlook on life was always cheery. He loved a joke and was ever ready with a witty repartee.

J. S. S. BRAME.

## NICHOLAS ALEXANDER ANFILOGOFF.

MANY members of the Institute received a great shock when they learned of the sudden death of Nicholas Alexander Anfilogoff on the 27th January, 1940. Only a few hours before, many of his friends had met him in his normal exuberant health at the Institute's luncheon.

Nicholas Anfilogoff was 65, but his physical and mental activities were those of a younger man.

He was born in Riga, and in due course became an undergraduate of the Russian Imperial Technical Institute in Moscow, where he distinguished himself as a Gold Medallist.

He was attracted, as were so many Russian chemists, to the petroleum industry, which in those days was better developed in Russia than in other countries. After gaining some refinery experience with the Rilsky Petroleum Co., and some knowledge of production and storage problems

by a stay in Baku, Anfilogoff decided to come to London. He arrived in 1894, being then only twenty, and obtained work with Dr. Dvorkovitz, a pioneer petroleum consultant, who up to ten or so years ago was a familiar figure in the precincts of Great St. Helen's. He then joined the European Petroleum Co., and after a few years started his long career at Thames Haven, where the Rumanian Oil Trust Refinery was operating. In those days he was much interested in the chemistry of petroleum, and carried out some investigational work himself. He has often told me of his early discovery of aromatics in East Indian petroleum, and of his many experiments in refining gasoline and kerosine by methods other than the then standard sulphuric acid and soda treatment. For some reason he seems never to have published any of his work. In the name index of the Science of Petroleum his does not appear, but nevertheless his memory will long be cherished by the many who knew him or who heard him at meetings of the Institute, discussing with vigour and emphasis points in a paper with which he did not agree.

His career at Thames Haven was marked by extensive developments in the storage installation and in the refinery, which was often called upon to work up a variety of crudes at short notice and never failed to do so. This is a striking testimony to his ability in design and management.

In 1930 he became a Director of the London & Coastal Oil Wharves, Ltd., and undertook the responsibility for the design and construction of a second great storage plant.

He was an original member of the Institute, and a regular and enthusiastic attendant at the meetings. He frequently took part in the discussions, and regularly attended the annual dinners. He was, moreover, a Fellow of the Institute of Chemistry, and a member of the Institutions of Mechanical and Chemical Engineers. Such combinations of activities are nowadays rare. But in the Institute's register he appeared as he was always known to his many friends and as he will long be remembered, simply as Anfilogoff.

J. KEWLEY.

## Dr. J. A. L. HENDERSON.

JAMES ALEXANDER LEO HENDERSON died at his home in London in his sixty-sixth year on 4th February, 1940.

He graduated from the Royal School of Mines, Freiberg, Saxony, with first-class honours, and proceeded to the University of Leipzig. In 1898 he gained the Ph.D. at the latter University for his valuable work on "Certain Transvaal Norites, Gabbros and Pyroxenites and other South African Rocks"—a work to which references were made in the geology of South Africa, where its value was subsequently most appreciated by economic geologists.

His professional activities carried him around the world in connection with the widespread interests of his father, the late J. C. A. Henderson. In addition to the mining investigations and developments in South Africa, Australia, New Zealand, the United States, Canada and Europe, Dr. Henderson was active in the establishment of the water-works for Lorenço Marques and the Tasmanian Timber Corporation.

In 1908 Dr. Henderson became particularly interested in the development of oil within the British Empire, and was largely responsible for the organization of the Maritime Oilfields, Ltd., to undertake exploration in New Brunswick, Canada. As is so often the case, there were differences of opinion in the geological deductions, but the first results obtained by drilling in this enterprise confirmed his views, and resulted in the constant supply of natural gas to Moncton during the last 30 years and the production of high-grade oil from the wells. These natural products have made New Brunswick Gas and Oilfields, Ltd., the success he had anticipated.

Whilst, as Vice-Chairman of the Holding and Operating Companies, in addition to being their technical adviser, his life became chiefly concentrated on New Brunswick, he maintained throughout an active interest in the development of oil in other parts of the British Empire.

In 1918 he paid particular attention to Trinidad, and, although there will always be many claims to the discovery of new and important sources of oil, his work in connection with the Apex (Trinidad) Oilfields, Ltd., played a large part in, and was largely responsible for, the early success of what was later to become the largest individual producer in Trinidad. In addition to his other work, he continued as Consultant to that Company until his death.

During his career Dr. Henderson took every opportunity to visit and study the many oilfields of California, Oklahoma, and elsewhere, and he had a particularly wide knowledge and appreciation of progress in geological and technical matters relating to the petroleum industry in many countries.

He was a founder-member of the Institute and for twenty-eight years had been a member of the Council of the Institute of Mining and Metallurgy, which he joined in 1899. He was also a member of many well-known technical and other societies in England and elsewhere.

We honour him as a colleague who, throughout his career, displayed those characteristics which, in scientific men, class them as great, not for any epoch-making discoveries, but for their tolerance, willingness to learn from the experience of others, and keenness to discuss the many scientific problems on all and every occasion. His passing will be sadly felt by a large number of friends at home and abroad.

Many of his colleagues who read this will recollect with pleasure the discussions and arguments, lasting into the early hours of the morning, which, due to him, were interesting, enjoyable, and fruitful, whatever the scientific disagreement might have been.